Synthesis of Cordierite by Complexing Agent-assisted Sol–Gel Procedure

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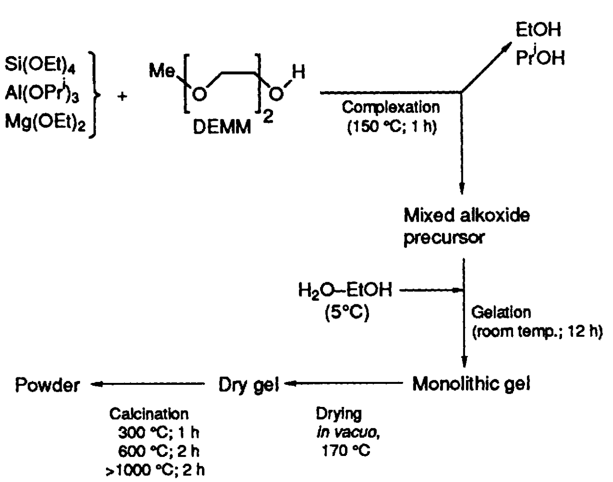
The amount of diethylene glycol monomethyl ether as solvent is critical in determining the reaction route in cordierite synthesis by the sol–gel procedure.

The sol–gel procedure has made it possible to produce ceramic materials of high purity and with superior properties at lower temperature than conventional methods. However, multi-component systems generally need precise control of synthetic conditions because the chemical properties of the individual components are often very different. Cordierite ($Mg_2Al_4Si_5O_{18}$), which is a representative ternary oxide, is an indispensable material for the honeycomb support of catalysts in automobile exhaust gas treatment and is also a promising material for electric applications. Recently, several reports have appeared on sol–gel syntheses of cordierite[1—5] at low temperatures. Since silicon alkoxides are generally hydrolysed much more slowly than aluminium and magnesium alkoxides, it is impossible to obtain a homogeneous precursor gel by simple mixing of the starting alkoxides followed by hydrolysis of the mixture. Accordingly, the synthetic procedure generally involves the partial hydrolysis of tetraethyl orthosilicate with dilute hydrochloric acid prior to addition of the other alkoxides as a key step, careful control of the hydrolysis conditions being needed.

Some of us have reported the regulation of the structure of iron oxide supported on a metal oxide by use of citric acid.[6] Our fundamental idea for structural regulation has been to control the inorganic condensation–polymerization by an organic complexing agent. We expected that particular organic compounds would lead to formation of the appropriate precursors for certain mixed oxides. This communication deals with a simple low-temperature synthesis of cordierite by the sol–gel procedure using a complexing agent as solvent.

The starting materials used in this study were commercial tetraethyl orthosilicate, aluminium isopropoxide, and magne-



Scheme 1. Synthesis of cordierite.

Table 1. Effect of the proportion of DEMM on the components of the calcined powders.[a]

Calcination Temp./°C	**a** (2 equiv.)	**b** (1.5)	**c** (1)	**d** (0.8)	**e** (0.67)	**f** (0.5)	**g** (0.25)
1000	α-C,μ-C	α-C,μ-C	α-C,μ-C	α-C,μ-C	β-Q,Spn	β-Q,Spn	Spn(broad)
1100	α-C	α-C	α-C	α-C	β-Q,Spn α-C	β-Q,Spn	Spn
1200	α-C	α-C	α-C	α-C	α-Q,Sap Cb,α-C	α-Q,Sap Cb	Sap
1300	α-C	α-C	α-C	α-C	α-C,Sap	α-C,Sap	α-C,Sap
1400	α-C	α-C	α-C	α-C	α-C	α-C	α-C

[a] α- or μ-C = α- or μ-cordierite, α- or β-Q = α- or β-quartz, Spn = spinel ($MgAl_2O_4$), Sap = sapphirine ($Mg_{3.5}Al_9Si_{1.5}O_{20}$), Cb = cristobalite.

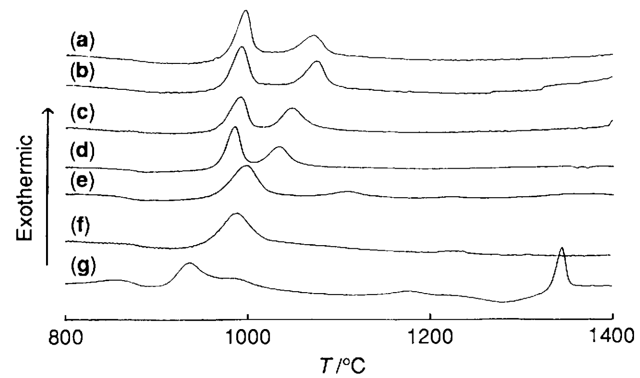


Figure 1. DTA of the dry gel from solutions with various amounts of DEMM. See Table 1 for (**a**)—(**g**).

sium ethoxide. Diethylene glycol monomethyl ether (DEMM) purchased from Tokyo Kasei, containing *ca.* 300 ppm of water according to Karl Fischer's method, was used as solvent without purification. The molar ratio of DEMM to the total amount of alkoxy substituents of the alkoxides was varied from 2:1 (**a**) to 0.25:1 (**g**). The synthetic procedure is illustrated in Scheme 1. The reactions were carried out under an ambient atmosphere. In the complexation step in Scheme 1, namely alcohol exchange of the alkoxides with DEMM, the liberated alcohols were distilled out of the system. The distillates from the reaction mixture during the complexation step contained all the alcohols expected to be generated according to equation (1). It is noteworthy that magnesium ethoxide, which does not show synthetically practical solubilities in common alcohols, readily dissolved in DEMM on alcohol exchange.

$$M(OR)_n + xR'OH \rightarrow M(OR)_{n-x}(OR')_x + xROH \uparrow \qquad (1)$$

$$M(OR)_n = Si(OEt)_4,\ Al(OPr^i)_3,\ Mg(OEt)_2;$$
$$R'OH = Me(OCH_2CH_2)_2OH$$

Table 1 shows the components of the powders after calcination at 1000—1400 °C for 2 h which were analysed by XRD. For samples (**a**)—(**g**) the components changed drastically depending on the amount of DEMM. Below 1200 °C, samples (**f**) and (**g**) with less than 0.5 equiv. DEMM gave no cordierite, but gave mixtures of spinel ($MgAl_2O_4$), quartz, sapphirine ($Mg_{3.5}Al_9Si_{1.5}O_{20}$) *etc.* On the other hand, samples (**a**)—(**d**) with 0.8—2 equiv. of DEMM gave α-cordierite as the main component at 1000 °C, becoming single-phase α-cordierite above 1100 °C. The samples synthesized from a mixed solvent of DEMM and diethylene glycol dimethyl ether in various proportions gave similar results depending on the amount of DEMM.

Figure 1 shows the differential thermal analysis (DTA) curves of the dry gels of (**a**)—(**g**). DTA curves of (**a**)—(**d**) with 0.8—2 equiv. of DEMM gave two distinct exothermic peaks near 990 and 1035—1070 °C. Because of resemblance with the reported result[2] these peaks are respectively assigned to the phase transition to μ-cordierite and that from μ-cordierite to α-cordierite. In contrast, samples (**e**)—(**g**) show quite different patterns.

These results have shown that there are mainly two routes from alkoxide-derived gels to α-cordierite and that only the amount of DEMM is critical in determining which route is taken. These differences in reaction pathway can be explained in terms of differences in homogeneity of the precursor gel. It is well known that magnesium halides or Grignard reagents form complexes with ethers used as solvents.[7] Moreover, *X*-ray structural analysis of a tetrameric magnesium polycation containing methoxyethanolato ligands showed co-ordination of magnesium by both oxygen atoms of the ligand.[8] Similar co-ordination has also been reported for several aluminium complexes.[9,10] Accordingly, we assume that DEMM decreases the hydrolysis rate of the Mg and Al alkoxides because the alkoxo-bound DEMM occupies an additional co-ordination site at magnesium or aluminium. Furthermore, DEMM binding to silicon may trap magnesium or aluminium to assist oxo-bridged-bond formation by slow hydrolysis with the trace amount of water in DEMM or moisture in the air.

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