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Formation of a novel type of reverse microemulsion system and its application in synthesis of the nanostructured $La_{0.95}Ba_{0.05}MnAl_{11}O_{19}$ catalyst†

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In the study, a novel microemulsion system, consisting of water, iso-propanol and n-butanol, was developed to synthesize the nanostructured $La_{0.95}Ba_{0.05}MnAl_{11}O_{19}$ catalyst with high surface area and catalytic activity for methane combustion.

Recently, catalytic combustion has attracted considerable attention due to its potential application for burning natural gas in gas turbines with extremely low levels of NO_x emissions.[1] The main challenge in the area is to select and synthesize catalytic materials with high thermal stability and high activity. Among them, catalysts based on barium or lanthanum hexaaluminate have received particular attention.[2] Arai *et al*. have synthesized a substituted barium hexaaluminate with high surface area and high activity using the sol–gel method.[3] Recently, nanostructured $BaAl_{12}O_{19}$ and Ce/$BaAl_{12}O_{19}$ have been synthesized in a reverse microemulsion-mediated sol–gel process by Ying *et al*, which have the highest surface areas obtained so far and excellent methane combustion activity.[4] However, nanostructured hexaaluminate catalysts are very difficult to synthesize, due to serious agglomeration and growth of the particles. In this work, a novel reverse microemulsion system was developed, which consisted of water, hydrophilic iso-propanol and half-hydrophobic n-butanol (W/iP/nB). The nanostructured $La_{0.95}Ba_{0.05}MnAl_{11}O_{19}$ catalyst was also synthesized in the system. The novel reverse microemulsion system could be potentially reused for preparation of the catalyst, and the preparation procedure is also simplified.

Typically, the system was composed of 5–20 vol.% water, 5–20 vol.% iso-propanol and 60–90 vol.% n-butanol. To prepare the microemulsion, the appropriate amounts of water, iso-propanol and n-butanol were mixed and then stirred until the emulsion became transparent. The $La_{0.95}Ba_{0.05}MnAl_{11}O_{19}$ catalysts were synthesized by hydrolysis of $Ba(iso\text{-}OPr)_2$ and $Al(iso\text{-}OPr)_3$ in the reverse microemulsion system, which consisted of an aqueous solution of stoichiometric $La(NO_3)_3$ and $Mn(NO_3)_2$/iso-propanol/n-butanol.‡ The stoichiometric amounts of $Al(iso\text{-}OPr)_3$ and $Ba(iso\text{-}OPr)_2$ were dissolved in iso-propanol, and the alkoxide solution was added to the ternary solvent system to hydrolyse and polycondense. The obtained sample was directly transferred to an autoclave for removing the solvent with supercritical drying (290 °C, 6.0 MPa). After drying, the sample was calcined at 1200 °C for 2 h. The structure property and phase behavior of the water in the system were investigated by means of FT-IR §, NMR ¶, electric conductivity (EC) ‖, laser light scatting granulometer **. The morphology, crystal structure and texture property of the catalyst were characterized by TEM, XRD and N_2-adsorption *etc*. ††. The catalytic activity over the catalyst for methane combustion was measured in a fixed reactor which is described elsewhere.[5]

Fig. 1a gives the wave number of $\nu_{O\text{–}D}$ vibration for D_2O *vs*. volume fraction of water in the ternary system, and Fig. 1b (ESI†) gives the IR spectrum of pure H_2O. The result of IR measurement shows that the $\nu_{O\text{–}D}$ band shifts to higher frequency with increasing *V*. The blue shift of the $\nu_{O\text{–}D}$ band indicates that hydrogen bonds between water molecules become stronger with increasing of water content.

As shown in Fig. 2, δ_{H2O} at $V = 0.02$ is *ca*. 4.49, and δ_{H2O} gradually shifts to low field with increasing *V*. δ_{H2O} is electron density of H^1 in H_2O, which denotes the polarization behavior of water molecules. The larger the value of δ_{H2O}, the stronger the polarization and the hydrogen-bonding interaction of the water molecules are.[6] This also indicates that the hydrogen bonds of water become stronger with increasing of water content in the ternary system. It has been reported that ethanol molecules exist as self-associated aggregates through hydrogen bonds between ethanol molecules in nonpolar solvents.[6,7] Besides, Mizuno *et al*.[8,9] investigated the self-association behavior of ethanol molecules in an aqueous solution by NMR and FT-IR. Their results showed that self-association of ethanol molecules in an aqueous solution occurs over the whole range of ethanol concentration, and the hydrogen bonds become stronger with increase of the size of the ethanol aggregates, due to a cooperative effect of hydrogen bonding. We could believe that the strengthening of hydrogen bonds between

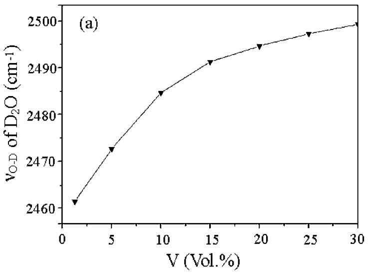

Fig. 1 Wave number ($\nu_{O\text{–}D}$) of O–D stretching vibration of D_2O *vs*. volume percent (*V*, vol.%) of water in the water/iso-propanol/n-butanol system.

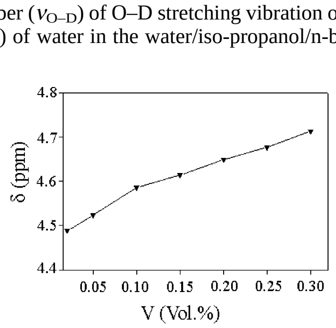

Fig. 2 Chemical shift (*δ*) of ^1H-NMR as a function of volume percent (*V*) of water in the H_2O/iso-propanol/n-butanol system.

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† Electronic supplementary information (ESI) available: Table 1, Figs. 1b, 5, 6 and 7. See http://www.rsc.org/suppdata/cc/b4/b404133j/

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water molecules is due to the formation of self-associated water aggregates. The size of self-associated water aggregates increases with increase of water content (V), and the hydrogen bonds become stronger with increase of the size of water aggregates.

The discrete droplets and connected clusters could be easily distinguished from the conductivity variation for a nonionic microemulsion.[10] Fig. 3 gives the variation of electric conductivity (κ) as a function of volume fraction (V) of 0.1 M $Mn(NO_3)_2$ aqueous solution in the 0.1 M $Mn(NO_3)_2$ aqueous solution/iso-propanol/n-butanol system. 0.1 M $Mn(NO_3)_2$ aqueous solution, instead of pure water, was used to increase the electric conductivity of the system. For the pure water system, the electric conductivity follows a linear correlation with V. For the ternary system, however, $k \sim V$ curve is nonlinear when V is low. There exists a critical point of V_0^c (0.15vol.%) in the $k \sim V$ curve. When $V \leq V_0^c$, the conducting behavior of the system could be ascribed to electrophoretic movement of the dispersed globules, as suggested by Peyrelasse *et al.*[11] When $V > V_0^c$, the conducting behavior may result from a progressive interlinking and clustering processes of aqueous droplets, similar to the conducting behavior of the nonionic microemulsion reported by Lagourette *et al.*[12] The results also suggest that water aggregates or water clusters are really present in the ternary solvent system.

A laser light scattering apparatus was used to measure the size of water droplets in the normal reverse microemulsion. The results are shown in Fig. 4. The size of water droplet at 5vol.% H_2O in the water/iso-octane/n-hexanol/$C_{13}EO_6$ microemulsion ranged from 14 to 120 nm, as shown in Fig. 4 (a). However, the method failed in measuring the size of water aggregates in the W/iP/nB system. Therefore, we measured the colloidal particles formed in the novel system, in order to evaluate the size of the "micelle" for the W/iP/nB system. The $Al(OH)_3$ colloidal particles, produced by hydrolysis of $Al(iso\text{-}OC_3H_7)_3$ in the system with 12.5 vol.% water content, ranged from 226 nm to 329 nm, as shown in Fig. 4 (b). Generally, the size of the particles formed in reverse microemulsion is larger than that of the corresponding water droplets which act as nanoreactors.[13,14] Therefore, the average size of the water droplets in the W/iP/nB system should be smaller than 267 nm. However, the diameter of the $Al(OH)_3$ gel particles formed in pure water is *ca.* 5962 nm (Fig. 4c), much larger than that (267 nm) from the ternary system.

We tentatively conclude that a novel reverse microemulsion system was formed by water, iso-propanol and n-butanol, just as for the familiar nonionic reverse microemulsion system. Hydrophilic iso-propanol was used to break hydrogen bonds between water molecules, so that the self-associated water aggregates become small. Some amphiphilic n-butanol molecules acted as surfactant to decrease the surface tension of the water droplets, and most of the n-butanol molecules acted as a disperse medium.

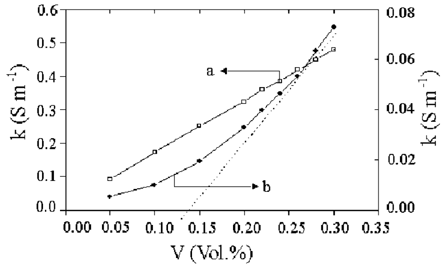

Fig. 3 Electric conductivity (κ) *vs.* volume percent (V) of 0.1M $Mn(NO_3)_2$ aqueous solution in the different systems: (a) Pure water system, (b) Water/iso-propanol/n-butanol system.

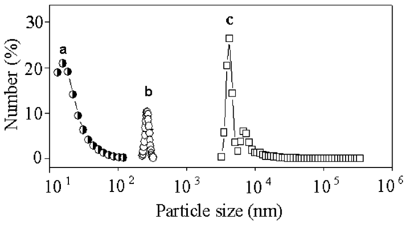

Fig. 4 The micelle size of the conventional microemulsion and size of $Al(OH)_3$ colloidal particles prepared by hydrolysis of Al(iso-PrO)$_3$ in different systems (a) Micelle size at V = 5.0vol.% in water/iso-octane/n-hexanol/$C_{13}EO_6$ microemulsion, (b) V = 12.5vol.% in the water/iso-propanol/butanol system, (c) in pure water system.

The $La_{0.95}Ba_{0.05}MnAl_{11}O_{19}$ catalysts for high-temperature combustion of methane was synthesized in the novel system. The effect of the solvent ratio on the catalyst is given in Table 1 (ESI†). The XRD patterns and light-off curves of the catalyst are shown in Fig. 5 and 6 (ESI†). The catalyst has a surface area of 65 m^2g^{-1}, much higher than that (32 m^2g^{-1}) of the catalysts prepared in pure water. Under gas mixture of 1 vol.% CH_4 and 99 vol.% air at 48,000 h^{-1} (GHSV), $T_{10\%}$ (ignition temperature) and $T_{90\%}$ (complete combustion temperature) over the nanostructured $La_{0.95}Ba_{0.05}MnAl_{11}O_{19}$ catalyst were 420 and 650 °C, respectively, much lower than those ($T_{10\%}$ = 510, $T_{90\%}$ = 770 °C) of the catalyst prepared in pure water. XRD patterns revealed that the pure hexaaluminate phase was formed for the catalyst synthesized in the W/iP/nB system. However, the catalyst prepared in pure water contained a small amount of α-Al_2O_3 and $BaAl_2O_4$. Observed from TEM (Fig. 7 in ESI†), the catalyst synthesized in the W/iP/nB system is *ca.* 30 nm in size, much smaller than that (*ca.* 100 nm) prepared in a pure water system. We believe that its high catalytic activity could arise from formation of the nanostructured hexaaluminate particles, which could provide more active sites at the same content of manganese than the catalyst prepared in pure water system. The W/iP/nB reverse microemulsion provides a novel nanoreactor system for synthesis of the nanostructured catalyst.

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Notes and references

‡ Preparation conditions: water : PrOH : BuOH = 12.5 : 12.5 : 75 (vol.%), $M(OR)_x$: water = 1 : 100 (mole ratio).

§ FT-IR spectra were measured on a Bruker EQUINOX 55 FT-IR spectrometer equipped with a MCT detector. An amount of D_2O was added to the ternary system, and volume percent of D_2O in H_2O was kept at 4 vol %. The O–D stretching vibration band ($\nu_{O–D}$) of D_2O was used to investigate structure property and phase structure of water in the ternary system, because the O–H stretching vibration band ($\nu_{O–H}$) of water overlaps with that of iso-propanol and n-butanol.

¶ ^{1}H-NMR spectra were taken on a Bruker DRX-400FT nuclear magnetic resonance spectrometer operating at 400 MHz at 25 ± 0.1 °C. Me_4Si (TMS) dissolved in $CDCl_3$ was used as an external reference substance to determine the chemical shifts of ^{1}H-spectra.

‖ The electric conductivity measurements were taken with a LEICI Model DDS-11A conductometer using a cell 1.005 cm^{-1} constant.

** The size distribution of $Al(OH)_3$ colloidal particles (PSD) were measured with a Malvern Zeta sizer 1000 laser light scatting granulometer.

†† The morphology, crystal structure and texture property of the catalyst were characterized by TEM (JEOL model 200CX apparatus), XRD Rigaku DMAX-rB X-ray diffractometer and N_2-adsorption (Micromeritics ASAP 2010), respectively.

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