

PILLARED LAYERED MANGANESE OXIDE

Synthesis and redox properties

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Keggin ion-pillared buserite was prepared by ion-exchanging the hexylammonium ion-expanded buserite with Keggin ions, $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. The starting material was synthetic Na-buserite, which is a layered manganese oxide of composition $\text{Na}_4\text{Mn}_{14}\text{O}_{26}\cdot x\text{H}_2\text{O}$. The thermal and redox properties of this oxide and its pillared derivative were compared in O_2 , N_2 and H_2 environments using TG, DSC and XRD. The results indicated an improvement in thermal stability of pillared compound relative to Na-buserite in all gaseous environments. By using these compounds in catalysing the oxidation of ethane, it was found that they were very active for complete oxidation.

Keywords: manganese oxide, pillaring layered compounds, TG/DSC, X-ray diffraction

Introduction

Pillaring layered compounds with robust polyoxometallic oligomers is a new route to prepare microporous materials. Structure and properties of such assemblies can be mediated by controlling subtle guest–host interaction [1–4]. This area has received much attention due to the potential use of the resultant compounds in catalysis and adsorption. In this study, Na-buserite was used as the starting material for preparation of both hexylammonium ion-expanded and Keggin ion-pillared buserite, abbreviated as HEB and KPB, respectively. In HEB, the free interlayer spacing is expanded from 1.94 Å (in Na-buserite) to 12.94 Å [5]. This allows the ion-exchange process with Keggin ion of diameter 8.6 Å to proceed. Na-buserite is a non-stoichiometric layered manganese oxide (Fig. 1), with unit cell formula $\text{Na}_4\text{Mn}_{14}\text{O}_{26}\cdot x\text{H}_2\text{O}$ [6–7]. It is a major component of manganese nodules which occur abundantly in both marine and fresh water sediments. In a review article, Nitta [8] showed that manganese nodules were as effective as some commercial catalysts and adsorbents. In a previous report, we described the successful preparation of KPB with increased surface area and thermal stability [5]. The aim of this investigation was to characterize the thermal and

redox properties of both Na-buserite and KPB, so that their applications in catalysis could be explored.

Experimental procedures

The method for Na-buserite synthesis was adapted from Stähli [5, 9]. In the preparation of KPB, HEB instead of Na-buserite was used as the precursor for ion-exchange reaction with Keggin ion solution. The preparation method and structural characterization of both Na-buserite and KPB have been described [5].

Powder X-ray diffraction (XRD) patterns were obtained on a Philips PW 1840 automated powder diffractometer, using Ni-filtered $\text{CuK}\alpha$ radiation. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were carried out on a DuPont 951 TG analyzer and a NETZSCH DSC 404, respectively. Heating rates were $10 \text{ deg}\cdot\text{min}^{-1}$.

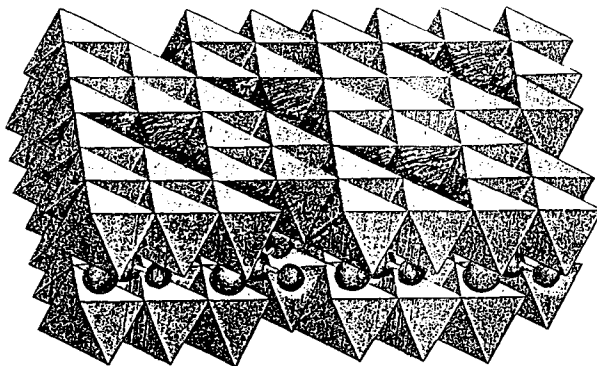


Fig. 1 Three-dimensional representation of Na-buserite structure

Catalytic experiments were carried out on a fixed-bed flow-through system with a diluted catalyst. Catalyst/ SiO_2 weight ratio $\approx 1/20$. The diluted catalyst was pre-treated at 370°C in an air flow overnight. The reactant was a mixture of ethane and air, with ethane/air mole ratios of 1/2 and 0.42/70 for oxydehydrogenation and combustion reactions, respectively. The products were analysed both on- and off-line by gas chromatography (GC).

Results

Synthesis of Na-buserite and KPB

XRD patterns of Na-buserite and KPB are shown in Figs 2a and 2b respectively. Na-buserite in its dehydrated state shows a first diffraction peak at $d = 7.1 \text{ \AA}$.

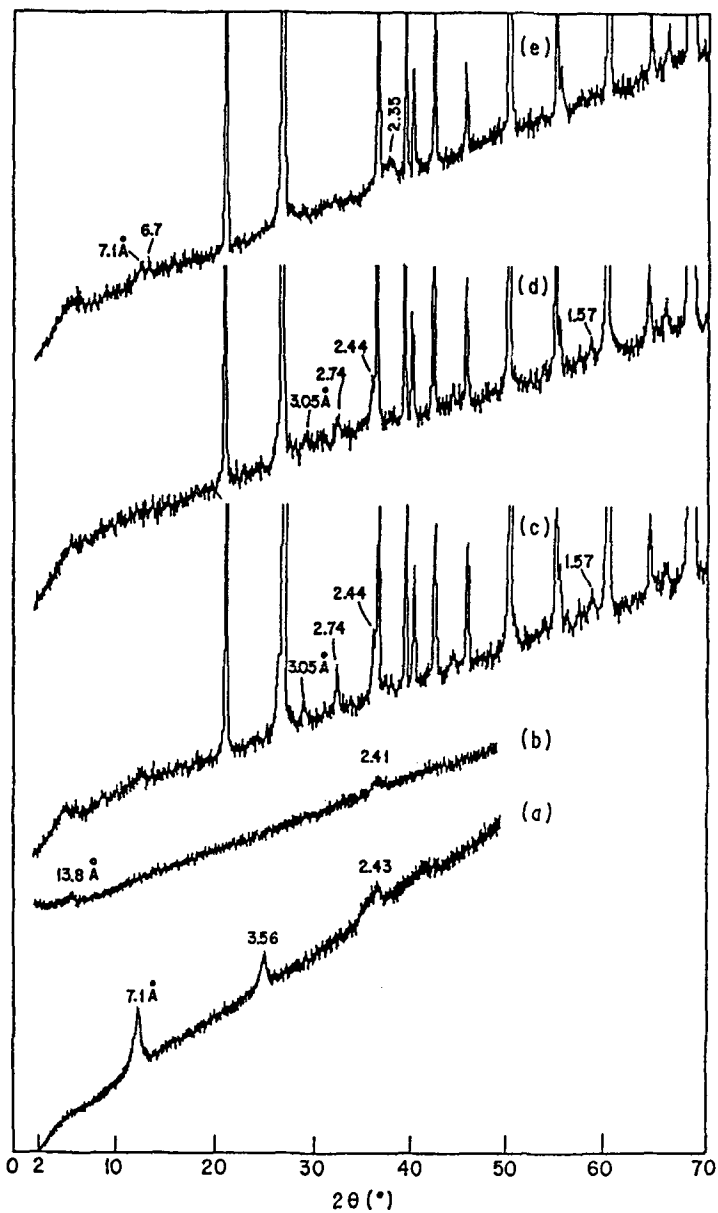


Fig. 2 XRD patterns of (a) Na-buserite, (b) KPb, (c) Na-buserite, after reaction at 370°C (contact time = $1.57 \times 10^{-3} \text{ g}\cdot\text{min}\cdot\text{ml}^{-1}$), (d) KPb, after reaction at 340°C (contact time = $1.41 \times 10^{-4} \text{ g}\cdot\text{min}\cdot\text{ml}^{-1}$), (e) Na-buserite, after reaction at 370°C (contact time = $1.41 \times 10^{-4} \text{ g}\cdot\text{min}\cdot\text{ml}^{-1}$)

When calcined in air at 300°C, this peak shifted to a lower d-spacing and all peaks became weaker and broadened (not shown). In KPB, the first diffraction peak appeared at $d = 13.8 \text{ \AA}$. Figs 2c to 2e will be described in later sections.

Redox properties

The redox properties of Na-buserite and KPB in different gaseous environments were studied by TG, DSC and XRD. TG and DTG curves for Na-buserite are shown in Figs 3A and 3B, respectively. The corresponding curves for KPB are shown in Figs 4A and 4B, respectively. DSC curves for Na-buserite and KPB are shown in Figs 3C and 4C, respectively. Peaks shown on these curves are related to temperatures of structural transformation. In Na-buserite, the Mn to O stoichiometry of the resultant compound(s) formed after each structural transformation can be determined from related weight losses on TG curves. These intermediate compounds can be further confirmed by XRD, and representative patterns for Na-buserite in a N_2 environment are shown in Fig. 5.

Peaks below $\approx 200^\circ\text{C}$ in the DTG curves are due to desorption of physisorbed and chemisorbed water, and the corresponding DSC curves show endothermic peaks for these processes. These will not be covered in subsequent sections.

For Na-buserite, the two weight losses in a N_2 environment correspond to endothermic peaks. During the first process, hollandite ($Na_2Mn_8O_{16}$) and Mn_2O_3 are formed. Mn_2O_3 is converted to Mn_3O_4 during the second process. Both hollandite and Mn_3O_4 in the final product gave XRD peaks of similar intensity. In a H_2 environment, however, the three weight losses are exothermic processes, which correspond to formation of Mn_2O_3 , Mn_3O_4 and MnO , respectively. In an O_2

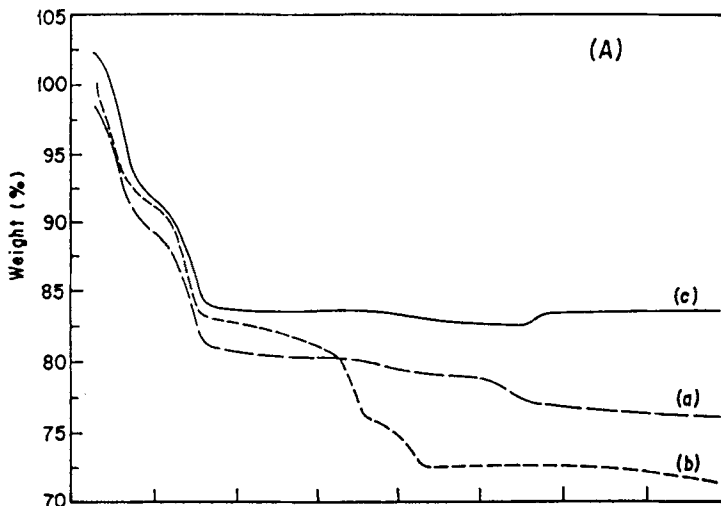


Fig. 3 (A) TG, (B) DTG and (C) DSC curves of Na-buserite in (a) N_2 , (b) $N_2:H_2 = 9:1$ (TG) or $Ar:H_2 = 49:1$ (DSC), and (c) O_2

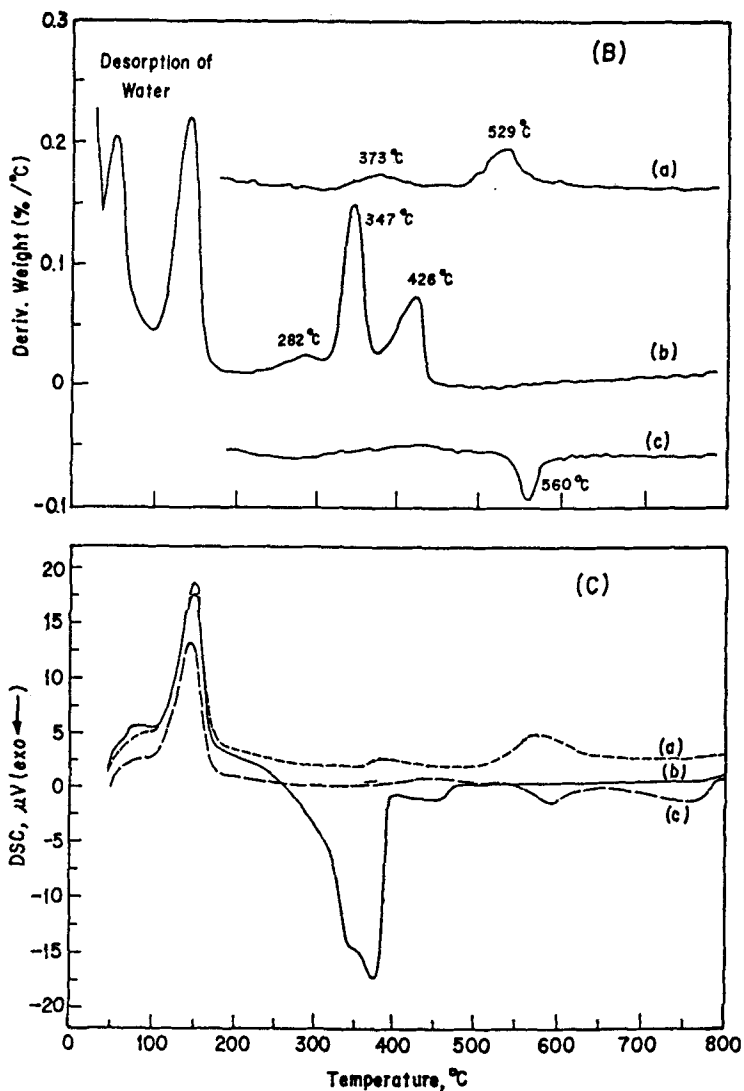


Fig. 3 Continued

environment, the sample shows a gradual endothermic weight loss between 300° and 500°C, which leads to formation of a compound(s) with Mn to O stoichiometry of $\text{Mn}_{14}\text{O}_{25.2}$. At $\approx 560^\circ\text{C}$, the sample is obviously gaining weight by an exothermic process. $\text{Na}_2\text{Mn}_5\text{O}_{10}$ is formed together with a smaller quantity of cryptomelane ($\text{Na}_{1-2}\text{Mn}_8\text{O}_{16}$). In addition, an exothermic peak at $\approx 750^\circ\text{C}$ is

prominent. XRD analysis of the Na-buserite sample calcined in air at 800°C showed that Mn_2O_3 and $Na_4Mn_9O_{18}$ were formed.

For KPB, two endothermic weight losses occurred in both N_2 and O_2 environments. XRD analysis of KPB calcined in air or N_2 at 700°C showed that either Mn_3O_4 or Mn_2O_3 formed. At 500°C however, the structure of KPB remained intact. In a $[H_2]$ environment, two DTG peaks occurred at 334°C and 448°C. The latter peak is much smaller and not always well resolved. The DSC curve of the

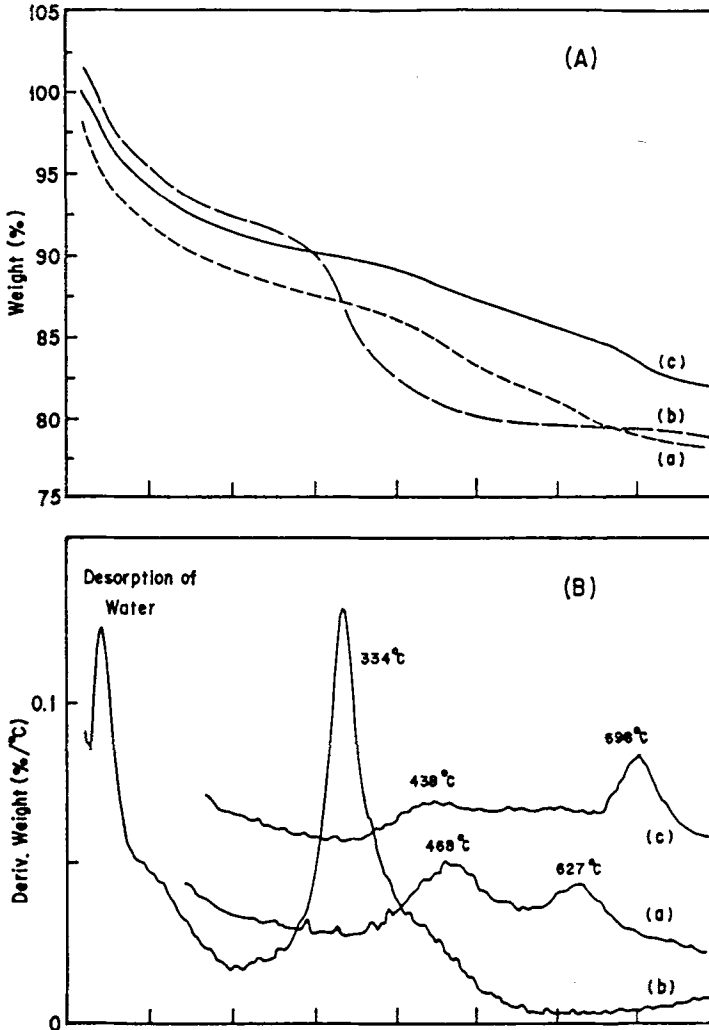


Fig. 4 (A) TG, (B) DTG and (C) DSC curves of KPB in (a) N_2 , (b) $N_2:H_2 = 9:1$ (TG) or $Ar:H_2 = 49:1$ (DSC), and (c) O_2

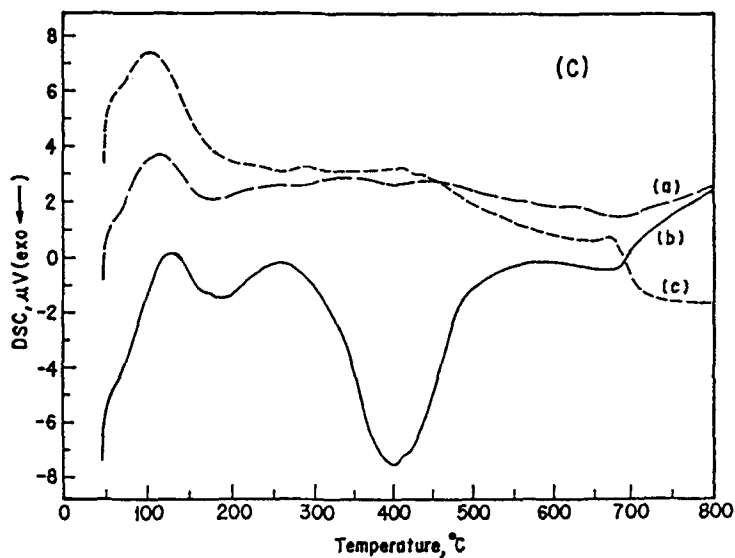
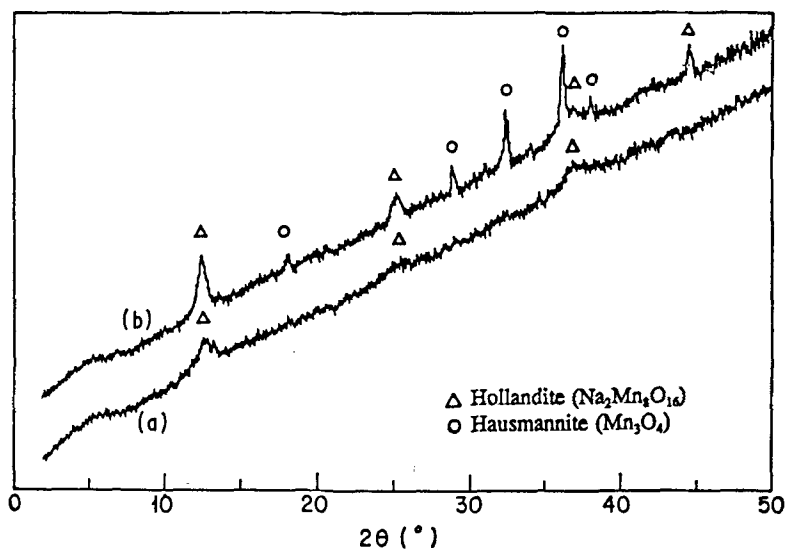


Fig. 4 Continued

Fig. 5 XRD patterns of Na-buserite in N_2 at (a) 320 $^{\circ}C$, (b) 550 $^{\circ}C$

sample shows an intense asymmetric exothermic peak at $\approx 402^{\circ}C$. From XRD analysis, the reduction product at 600 $^{\circ}C$ for 2 h was a mixture of Mn_3O_4 and

minor MnO. The two weight losses thus appear to be due to formation of Mn_3O_4 and MnO, respectively. The peak of the initial reduction product, Mn_2O_3 , cannot be resolved, but a shoulder is present near 300°C in the DTG curve. Other endothermic peaks also occur between 200°–400°C in all the DSC curves, although they are less prominent in an O_2 environment. In both H_2 and N_2 environments, an additional intense endothermic peak begins at 675° and 666°C, respectively.

Catalytic studies

Results of combustion and oxy-dehydrogenation of C_2H_6 over Na-buserite and KPB are shown in Table 1. In the oxy-dehydrogenation reaction, the conversion (per surface area) over Na-buserite catalyst increases as the reaction temperature was raised from 300° to 340°C. At both temperatures, the conversion does not vary significantly with time on stream. As the reaction temperature was raised to 370°C, the conversion decreased. A similar conversion was obtained with a fresh catalyst. The XRD pattern of the used catalyst (Fig. 2e) was similar to that of Na-

Table 1 Catalytic data for oxy-dehydrogenation and combustion of ethane at steady state

Sample	Temp./ °C	Contact time/ g·min·ml ⁻¹	Unit conv.* %/m ²	Selectivity/%		
				C ₂ H ₄	CO	CO ₂
Oxyde						
Na-B	300	1.41×10 ⁻⁴	0.4	8.8	tr	91.2
	340		1.1	7.4	1.5	91.1
	370		0.7	tr	4.5	95.5
Na-B	370	1.57×10 ⁻³	25.8	1.2	0.4	98.4
KPB	300	1.41×10 ⁻⁴	0.3	18.3	13.0	68.7
	340		11.3	20.8	3.6	75.6
Comb.						
Na-B	300	1.52×10 ⁻⁴	1.4	–	–	100
	340		4.8	–	–	100
	370		10.4	–	–	100
KPB	300	1.52×10 ⁻⁴	1.7	–	–	100
	340		6.1	–	–	100
	370		17.2	–	5.7	94.3

tr = trace

* BET surface areas for Na-buserite and KPB were 57 and 142 m²/g, respectively

buserite heated in a N_2 environment at a similar temperature, where Mn_2O_3 and hollandite were formed. The intense peaks (d values not indicated) are due to SiO_2 . However, if the initial contact time at $370^\circ C$ was increased more than 10-fold, e.g. from 1.41×10^{-4} to $1.57 \times 10^{-3} \text{ g} \cdot \text{min} \cdot \text{m}^{-1}$, the conversion increased sharply. The XRD pattern of the used catalyst showed that Mn_2O_3 or Mn_3O_4 were formed (Fig. 2c). The conversion over the KPB catalyst was lower than over Na-buserite at $300^\circ C$ with the same contact time. When the reaction temperature was increased to $340^\circ C$, conversion increased sharply as noted above for Na-buserite, with the formation of the same product (Fig. 2d). The selectivity of both C_2H_4 and CO over KPB catalyst at $300^\circ C$ were significantly higher than that over Na-buserite.

In the combustion reaction, conversion over Na-buserite catalyst was quite stable at each of the temperatures studied. XRD analysis of the used catalyst after reaction at $370^\circ C$ showed that the structure remained intact. However, the layered structure was highly disordered, as indicated by the diffuse nature of the XRD peaks. Over the KPB catalyst, conversion at each of the reaction temperatures decayed very slightly with time on stream at the initial stages of reaction. However, they maintained a stable value at steady state. Conversions at steady state were higher than for Na-buserite. CO_2 was the only product of reaction over Na-buserite. This was also true with KPB catalyst at steady state except at $370^\circ C$, where CO (4–8%) was also produced throughout the reaction. During the initial stages of reaction, C_2H_4 (at 340° and $370^\circ C$) and CO (at 300° and $340^\circ C$) were observed also.

Discussion

The interlayer free spacing of dehydrated Na-buserite is about 1.9 \AA , which corresponds to the diameter of Na^+ ions. Therefore, the basal thickness of the layer is 5.2 \AA . As the Na^+ ions are replaced by Keggin ions in KPB, the free spacing will increase to $\approx 8.6 \text{ \AA}$, which is the diameter of Keggin ions. This corresponds to an interlayer spacing of 13.8 \AA , i.e. basal thickness plus free spacing. The presence of this peak in the XRD pattern of KPB confirmed the successful synthesis of this pillared compound.

Na-buserite behaves differently in different gaseous environments. Hydrogen tends to reduce Na-buserite to MnO whereas oxygen and air tend to oxidize Na-buserite to $Na_2Mn_5O_{10}$ and cryptomelane. However, a reduced compound such as Mn_2O_3 can form at high temperature. In nitrogen, a mixture of reduced (Mn_3O_4) and oxidized (hollandite) compounds is formed. Therefore, the latter rearrangement process can be induced thermally and the oxygen required for the formation of oxidised compound must have come from the buserite structure itself. As a result, part of the structure is initially reduced to Mn_2O_3 . In an O_2 environment, the amount of reduced product formed is negligible, as would be expected.

KPB is relatively more stable than Na-buserite in all of the gaseous environments studied. Its structure is stable to $>600^{\circ}\text{C}$ in both O_2 and N_2 environments. In a H_2 environment, the KPB structure is relatively less stable. The endothermic processes occurring between 200°C – 400°C in all the gaseous environments are due mainly to slight loss of surface oxygen, since they are less prominent in an O_2 environment. Similarly, oxygen loss from the Na-buserite structure is also found to be least favoured in an O_2 environment. These processes are not likely to be due to chemical reactions or rearrangement, which were found to be exothermic in this study. Accordingly, the collapse in the KPB structure between 600°C – 700°C in both O_2 and N_2 environments may be the result of loss of lattice oxygen. The remaining exothermic process at temperature between 400°C – 470°C has been assigned to water loss, as a result of condensation between hydroxyls of the Keggin ions and the layers.

The products of structural transformation are different between Na-buserite and KPB in non-reducing environments, such as O_2 and N_2 . It is noted that compounds with tunnel structure such as hollandite and cryptomelane are present only in Na-buserite. These compounds consist of MnO_6 octahedra sharing edges to form double chains, which then linked by shared vertices forming $[2\times 2]$ channels [10]. In this case, the ion-exchange sites in the channels are occupied by Na^+ ions. As a result, formation of these compounds requires that the opposite layers in the Na-buserite come into close contact with each other at the intercationic spaces. This is possible since the interlayers are completely dehydrated and disordered at temperatures required for formation of the tunnel compounds ($>300^{\circ}\text{C}$). The layers will be significantly folded as a result of electrostatic attraction between the negatively charged layers and the cations [11]. In contrast, the Keggin ion pillars in the interlayers improve thermal stability of the layered structure by keeping the opposite layers further apart. In a H_2 environment, however, reduction of the layered structure probably begins at a temperature lower than that required for structural rearrangement to occur. The presence of aluminium, which is one of the components of Keggin ions, appears to stabilize the reduced manganese oxide phases. Therefore, reduction of Mn_3O_4 to MnO was not complete even at 600°C .

The catalytic performance of the catalysts was consistent with their redox behaviour. In an oxidation reaction, structural oxygen of various non-stoichiometric Mn oxides has been known to participate in the reaction [8]. If the structural oxygen consumed is not replenished, then reduction of the structure will occur. Since both catalysts are stable in combustion reactions, the redox behaviour of the structure is reversible. This is as expected since the reactant mixture is oxygen-rich in the combustion reaction. Besides, the maximum reaction temperature of 370°C is below the structural transformation temperature of 560°C in O_2 . The initial decrease in the conversion over KPB catalyst is due to occupation of active sites by partially oxidized products (C_2H_4 and CO) for further oxidation.

In the oxy-dehydrogenation reaction, Na-buserite catalyst deactivates at 370°C . This is caused by rearrangement of the layered structure into stoichiometric compounds of Mn_2O_3 and hollandite. These compounds are similar to

those observed in a N_2 environment. Therefore, the property of the reactant mixture surrounding the catalyst approaches that of N_2 . The Na-buserite catalyst is stable below 370°C , which is also consistent with the above suggestion. Hence, a decrease in the proportion of O_2 in the reactant mixture from combustion to oxydehydrogenation reaction renders it less oxidising. If the O_2 in the mixture is nearly or completely consumed in the reaction, then the structure will be reduced to Mn_2O_3 or Mn_3O_4 . This situation can occur at high reaction rates. In fact, the calculated O_2 conversion is nearly 100% at the conditions where structure reduction occurred. In this case, the partially oxidized products (C_2H_4 , CO) and even C_2H_6 can act as reducing agents. Since the small interlayer free spacing of Na-buserite only allowed reactions to occur on the external surfaces, this reductive disintegration of the catalyst increase the active surface area and accessibility to the internal sites. As a result, conversion increases sharply.

Unexpectedly, one can see that reductive disintegration of KPB catalyst occurred at 340°C , even though it is stable in N_2 to temperatures higher than 600°C . The reduction must originate from the interlayers since Na-buserite is stable at similar conditions. Therefore, it can be concluded that an O_2 -deficient environment is created in the interlayers of KPB at high reaction rate. By comparing the product selectivity of both catalysts, it is found that diffusion limitation is occurring in the interlayer. As 3.5 moles of O_2 is required to fully oxidize one mole of C_2H_6 , the rate of supply of O_2 into the interlayer by diffusion will not be sufficient to cope with the rate of consumption at higher reaction rate. Besides, C_2H_4 and CO produced in the interlayers are subjected to further oxidation by structural oxygen as they diffuse out of the interlayers. Once the interlayers are severely O_2 -deficient, the lattice oxygen will then be irreversibly consumed by C_2H_4 or CO, and reduction of the structure to Mn_2O_3 or Mn_3O_4 occurs.

Conclusion

This study demonstrates that the catalytic behaviour of Na-buserite and KPB can be elucidated by their thermal stability in various gaseous environments. The presence of Keggin ion pillars in the interlayers of buserite improved the thermal stability of the structure in both N_2 and O_2 environments. KPB is much less stable when either the external surface or the interlayer is in a reducing environment. Therefore, KPB is not suitable for use as a catalyst or a catalyst support for reactions such as CO hydrogenation. Instead, both Na-buserite and KPB are very active in complete oxidation reaction.

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Zusammenfassung — Keggin-ionengestütztes Buserit wurde durch Ionenaustausch von hexylammoniumionenerweitertem Buserit mit Keggin-Ionen $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ erhalten. Das Ausgangsmaterial war synthetisches Na-Buserit, ein schichtiges Manganoxid der Zusammensetzung $Na_4Mn_{14}O_{26} \cdot xH_2O$. In Sauerstoff-, Stickstoff- und Wasserstoffumgebung wurden mittels TG, DSC und Röntgendiffraktion die thermischen und Redox Eigenschaften dieses Oxides und der gestützten Derivate miteinander verglichen. Bei allen gasförmigen Umgebungen erweisen sich die gestützten Verbindungen thermisch stabiler als Na-Buserit. Bei der Anwendung dieser Verbindungen zur Katalyse der Oxidation von Ethan fand man, daß sie bezüglich einer vollständigen Oxidation sehr aktiv sind.