Catalysis Letters Vol. 100, Nos. 3–4, April 2005 (© 2005)
DOI: 10.1007/s10562-004-3463-4

Metal oxide catalysts for DME steam reforming: Ga_2O_3 and Ga_2O_3–Al_2O_3 catalysts

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Received 1 October 2004; accepted 4 December 2004

The steam reforming of dimethyl ether (DME) was performed on Ga_2O_3–Al_2O_3 mixed oxides prepared by sol–gel method. Ga_2O_3 significantly affects the catalytic performance with respect to the DME conversion and H_2 yield. The catalytic activity increases with the Ga concentration in Ga_2O_3–Al_2O_3 mixed oxides. It is very interesting that without the aid of an additional transition metal component, Ga_2O_3 and Ga_2O_3 containing Al_2O_3 mixed oxide system exhibit good activity in the reforming reaction. To the best of our knowledge, this is the first report that reveals the reforming ability of Ga_2O_3 for the production of H_2 from DME and/or methanol.

KEY WORDS: fuel cells; DME steam reforming; Ga_2O_3–Al_2O_3; mixed oxides.

1. Introduction

Recently, use of H_2 in fuel cells for automobiles and other applications has had a wide interest in the development of the technologies for on-board H_2 production from liquid fuels [1]. A variety of fuel processing systems have been developed to obtain H_2 from methanol and hydrocarbons such as natural gas, gasoline, etc. [1–5]. Lack of wide distribution network, comparatively low H_2 density, requirement of high temperature for the reforming process and the presence of sulfur compounds form some of the inherent drawbacks associated with these raw materials [1–5]. Hence, the advancement in this field requires the improvement of existing processes as well as finding new types of clean fuels for H_2 production. In pursuit of this goal, the steam reforming of dimethyl ether (DME) has had a growing interest in view of its applicability in the production of H_2 for fuel cell applications [6–9]. DME is relatively inert, noncorrosive and noncarcinogenic, which makes it a suitable candidate for reducing pollutants and providing cleaner air. At ambient conditions, DME is known to exist as gas and can be liquefied at slightly higher pressures, making its storage and transportation comparatively easy. These aspects of DME make it promising for employing in the reforming reactions and for the mobile use [6–9].

Partial oxidation and steam reforming are the primary methods used in reforming DME to produce hydrogen for use in fuel cells. There are many reports available on the partial oxidation of DME [10–13]. Compared to partial oxidation, the catalytic steam reforming of DME offers higher hydrogen concentrations in the crude reformate gas. Although there have been many patents on DME steam reforming, there are only three published articles in the literature [14–16]. Gavita *et al.* carried out DME steam reforming over a mechanical mixture of 12-tungstosilicoheteropolyacide deposited on γ-Al_2O_3 and Cu deposited on SiO_2 [15]. Various metals such as Cu, Pd, Pt, Rh, Ru, Au and their combinations supported on γ-Al_2O_3 for DME steam reforming has been reported very recently [16]. Since the DME steam reforming initially involves its hydrolysis to methanol followed by methanol steam reforming, the key technology required for this process is similar to the methanol steam reforming process [14–16]. A multi-component catalyst system in which one of the metals like Cu, Pd or Pt supported on an acidic mixed oxide is often used for such reactions. Alumina has been widely employed as a support in such reactions because its acidic property is favorable for hydrolysis of DME. Alumina in combination with other metal ions of comparable radii or similar oxidation state is expected to be more active [17–20]. For instance, the acidic sites can be modified by doping cations such as Ga to the alumina matrix. Due to the similarities in the oxidation states and/or ionic radii, isomorphous substitution can occur and thus solid solutions of the type M_I–O–M_{II} are formed. This leads to surface heterogeneity and as a result, such materials may find wider applications especially when multi reactions have to be performed. During our efforts to search for a new catalyst system having the composition $Cu/M_xAl_{10-x}O_{15}$ ($M = B^{3+}$, Ga^{3+}, Ce^{3+}, La^{3+} and Fe^{3+}), we observed that the

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1011-372X/05/0400–0247/0

support $Ga_xAl_{10-x}O_{15}$ exhibited good activity in the DME reforming reaction along with $Cu/Ga_xAl_{10-x}O_{15}$. In this short communication, we report the efficacy of $Ga_xAl_{10-x}O_{15}$ oxide system in the steam reforming of DME.

2. Experimental

A series of Ga_2O_3–Al_2O_3 mixed oxides as well as the simple oxides of Ga and Al were prepared by the sol–gel method using ethylene glycol as the solvent. Stoichiometric amounts of metal nitrate solutions were mixed and maintained at 353 K with continuous stirring for 12 h. The solvent was then removed by heating from 353–383 K under reduced pressure. The resulting gel was dried at 473 K followed by calcination at 773 K for 5 h. The catalyst samples are abbreviated as $Ga_xAl_{10-x}O_{15}$, where 'x' varies from 0 to 10. Note that $x = 0$ and 10 in the formula corresponds to pure Al_2O_3 and Ga_2O_3, respectively.

The catalysts were characterized by adopting various physico-chemical methods such as XRD, BET surface area and ammonia TPD. The powder X-ray diffraction patterns of all the catalyst compositions were recorded using a RINT2000 (Rigaku) equipped with Cu–Kα radiation with a Ni filter. The specific surface area of the various samples was measured according to the BET method by N_2 adsorption. The acidic property of each catalyst was characterized by NH_3–TPD. NH_3 was adsorbed at 313 K after pre-treatment at 773 K in a He stream. The desorbed NH_3 in flowing He gas was quantified by q-mass spectroscopy at temperatures from 313 K to 773 K at a ramp rate of 10 K/min.

The catalytic activity was performed in a fixed-bed flow quartz reactor using 150 mg of the catalyst over the temperature range of 473–673 K. The catalysts were heated under a N_2 flow (50 mL/min) for 30 min at 673 K prior to the catalytic activity estimation. The feed mixture that consisted of 1% DME diluted with N_2 and 3% water vapor was allowed to pass through the reactor at a flow rate of 50 mL/min (GHSV = 20,000 mL g^{-1} h^{-1}). The effluents were analyzed by online gas chromatography, namely an Aligent technology M-200H gas chromatograph (equipped with two thermal conductivity detectors and two capillary columns with a He carrier; a Poraplot Q column to separate CO_2, H_2O, HCHO, DME and methanol and a Molecular Sieve 5A column to separate CO and CH_4) and an Aligent micro GC 3000A gas chromatograph equipped with Molecular Sieve 5A column (Ar carrier) to analyze H_2. H_2, CO_2, methanol, CO, H_2O and traces of CH_4 were the only products detected under the present experimental conditions. The best performing catalysts were subjected to further investigation to ensure the validity of the results.

3. Results and discussion

3.1. Catalytic activity

Table 1 compares the catalytic activity data at 673 K for various compositions of Ga_2O_3–Al_2O_3 mixed oxides. The DME conversion and H_2 yield mainly depend on the Ga content. Figure 1 illustrates the effect of Ga concentration on DME conversion and H_2 yield at various temperatures for $Ga_xAl_{10-x}O_{15}$, where the H_2 yield is defined as the percentage of the maximum theoretical H_2 produced based on DME and water feed assuming that 1 mol of DME could react to form 6 mol of H_2. From the results, it is clear that simple Al_2O_3 is not a good choice for DME reforming although it catalyzes DME hydrolysis. An increase in the Ga_2O_3 loading resulted in an increase in the DME conversion and H_2 yield. The remarkable role of Ga_2O_3 in achieving a high DME conversion and H_2 yield is evidenced by comparing the activity data of pure Al_2O_3 with Ga_2O_3–Al_2O_3 mixed oxides having a low Ga_2O_3 content. For example, the introduction of 1 mol% Ga_2O_3 in Al_2O_3 displays an increase in the DME conversion from 23% to 48% and that of H_2 yield from nearly 0% to 18% at the reaction temperature of 673 K. With the further addition of Ga_2O_3, the conversion and H_2 yield improved to 65% and 42%, respectively. Thus, the introduction of a small amount of Ga_2O_3 dramatically enhances the catalytic activity.

It was observed that the DME conversion increases with increasing temperature and attains ~90–100% at 673 K in the case of pure Ga_2O_3 and $Ga_xAl_{10-x}O_{15}$ at $x \geq 4$. Even though, Ga_2O_3 is good for reforming, the conversion and H_2 yield of Ga_2O_3 was less than the most effiecient Ga_2O_3–Al_2O_3 (at $x = 8$ in $Ga_xAl_{10-x}O_{15}$) mixed oxide catalyst. A reasonable explanation for this improvement would be the formation of highly dispersed active Ga_2O_3 species strongly interacting with alumina. The concentration of CO and CO_2 expressed in terms of selectivity is also provided in table 1. The selectivity of CO (or CO_2) is expressed as the ratio of the concentration of CO (or CO_2) to the total concentration of the carbonaceous products (except DME) normalized to 100%. Pure Ga_2O_3 shows comparatively less CO selectivity. It was found that the H_2/CO ratio increases and the product mixture become enriched with H_2 as the Ga_2O_3 loading increases.

The stability of the catalysts in terms of the DME conversion and H_2 yield were studied as a function of time on stream at 673 K and a space velocity of 10,000 h^{-1} on Ga_2O_3 and $Ga_8Al_2O_{15}$ are shown in figure 2. The conversion of DME as well as the H_2 yield slightly decreased with the reaction time on Ga_2O_3. A stable performance of DME conversion was observed on $Ga_8Al_2O_{15}$ over a time period of 6 h. Moreover, the H_2 yield also remained constant although a slight drop was found in the first 2 h. It is expected that the stable activity for DME steam reforming can be sustained for a

Table 1

Physico-chemical characterization and catalytic activity data of $Ga_xAl_{10-x}O_{15}$

Composition	Surface area (m^2/g)	Relative acidity (a.u)	DME Conversion (%)	H_2 yield (%)	Selectivity, %		
					CO_2	CO	MeOH
Al_2O_3	106	1.0	24	1	0	9	91
$Ga_{0.1}Al_{9.9}O_{15}$	123	2.0	48	18	3	50	47
$Ga_{0.5}Al_{9.5}O_{15}$	75	1.4	64	41	16	69	15
$Ga_2Al_8O_{15}$	55	1.2	87	61	28	70	2
$Ga_4Al_6O_{15}$	100	1.3	99	71	28	72	0
$Ga_6Al_4O_{15}$	92	1.3	95	70	44	56	0
$Ga_8Al_2O_{15}$	100	17	100	74	46	54	0
Ga_2O_3	54	1.0	93	64	57	43	0

Reaction conditions: 673 K, GHSV = 20000 h^{-1} mL (g cat)$^{-1}$, Feed composition; 1% DME and 3% H_2O diluted with N_2.

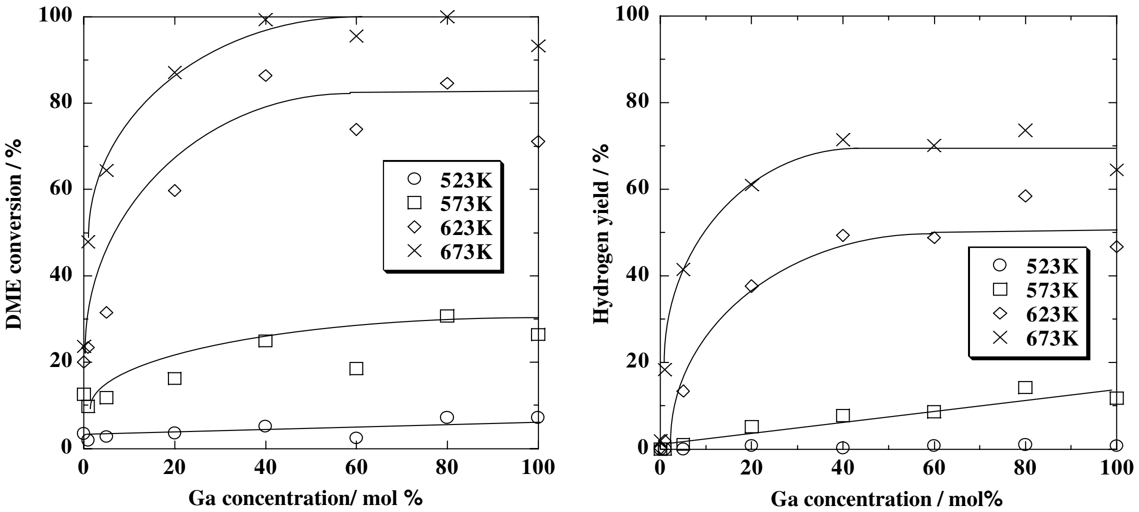

Figure 1. Ga concentration dependence of DME conversion (left panel) and H_2 yield (right panel) at temperatures between 523 and 673 K on $Ga_xAl_{10-x}O_{15}$. Reaction was carried out at a gas hourly space velocity of 20000 h^{-1} using the feed composition of 1% DME and 3% H_2O (diluted with N_2).

long period, although the examined period was just 6 h. Figure 3 shows the effect of the space velocity on the conversion of DME and the yield to H_2 on $Ga_8Al_2O_{15}$ and Ga_2O_3 at 673 K. In the space velocity range of 5000–25000 h^{-1}, complete conversion of the DME was observed on $Ga_8Al_2O_{15}$. However, the H_2 yield decreased as the space velocity increased. This is due to the contribution of H_2 from the water gas shift reaction and is evidenced from the increase in the CO_2 concentration as the space velocity decreased (not shown). In order to test the performance of catalysts at higher DME concentration, the steam reforming reaction was carried out on a few selected compositions. A feed composition of 10% DME, 30% water and 60% N_2 at GHSV = 15,000 mL g^{-1} h^{-1} was used. It was found that the rate of H_2 production increases indicating that the catalysts are active even at high DME concentration.

The mechanism of steam reforming of DME can be very complex over the Ga_2O_3–Al_2O_3 catalyst system. There might be several processes catalyzed by Ga_2O_3 under the reaction conditions of DME steam reforming, such as DME hydrolysis, methanol decomposition, methanol steam reforming, direct DME decomposition and water gas shift reaction. For a better understanding of the reaction paths, tests of simple steam reforming and decomposition of methanol as well as direct decomposition of DME were carried out on selected catalysts. It has to be noted that both the methanol reactions and the decomposition of DME were carried out in a similar reaction conditions applied for the DME steam reforming. The methanol steam reforming was performed using a methanol:water feed ratio of 1:2. For the decomposition reactions, 1% DME (or 1% methanol) in a flow of N_2 was passed as the reactant.

Figure 4 compares the activity data for both steam reforming and decomposition reactions of DME for the catalyst $Ga_8Al_2O_{15}$. In the direct DME decomposition tests, lower conversions of DME with very less H_2 yield were observed at all temperatures than under the steam reforming of DME. Thus, it is possible that part of the

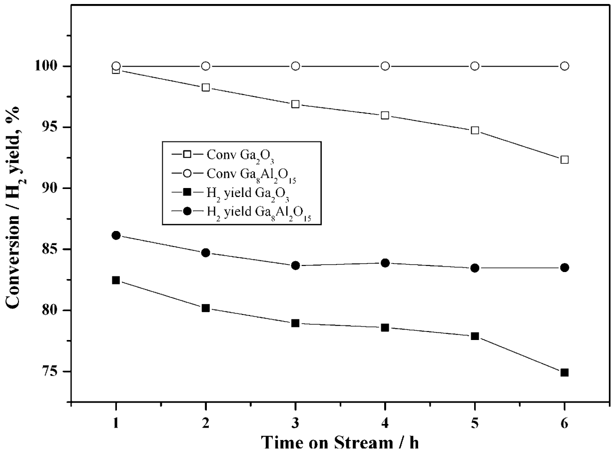

Figure 2. Time dependence of DME conversion and H_2 yield on $Ga_8Al_2O_{15}$ and Ga_2O_3 catalysts at 673 K. DME steam reforming was carried out with a feed composition of 1% DME and 3% H_2O (diluted with N_2) at a gas hourly space velocity of 10000 h^{-1}.

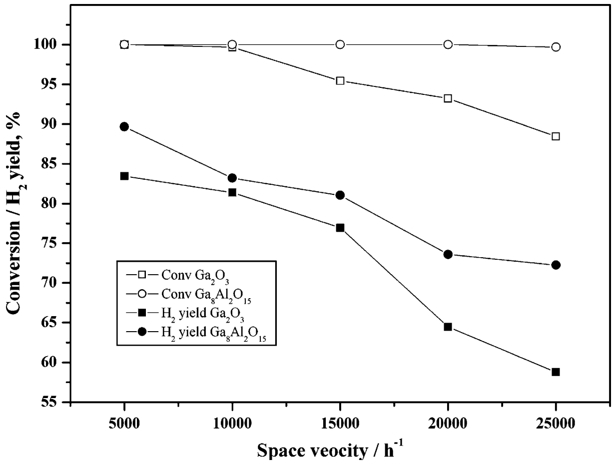

Figure 3. Effect of gas hourly space velocity (GHSV) on DME conversion and H_2 yield on $Ga_8Al_2O_{15}$ and Ga_2O_3 catalysts at 673 K. DME steam reforming was carried out with a feed composition of 1% DME and 3% H_2O (diluted with N_2).

DME can be converted into CO_x and H_2 *via* its direct decomposition during the steam reforming reaction. However, the absence of CH_4 in the steam reforming reaction indicates that the direct decomposition of DME could be suppressed to a great extent in the presence of steam. Therefore, the steam reforming of DME over the present catalyst system is mainly accomplished *via* successive two step reactions as reported in the literature [15,16]. The first step is the hydration of DME to produce methanol:

$$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH \qquad (1)$$

This reaction is followed by steam reforming of methanol:

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \qquad (2)$$

In our experiments, a significant amount of CO in the product (table 1) revealed that the steam reforming of methanol proceeds through various reactions such as direct steam reforming, decomposition and water gas shift (WGS) reactions over the Ga_2O_3–Al_2O_3 catalyst system. Figure 5 shows the comparison of steam reforming and decomposition of methanol for the catalyst $Ga_8Al_2O_{15}$. In both the cases, noticeable amounts of CO_x and H_2 were observed at $T \geq 573$ K. As expected, the decomposition of methanol produced a larger proportion of CO and CH_4. On the other hand, the steam reforming of methanol produced high selectivity in the CO_2 among the products. Also, there was no methane formation observed under the steam reforming condition. It is noted that the H_2 yield was greatly improved in the presence of steam in comparison with the simple decomposition reaction of methanol. These results indicate that the CO produced in the decomposition reaction is partly converted to CO_2 and H_2 *via* water gas shift reaction. Therefore, the methanol steam reaction in equation 2 can be considered as a combination of methanol decomposition (equation 3) and water gas shift reaction (equation 4).

$$CH_3OH \rightarrow 2H_2 + CO \qquad (3)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (4)$$

According to this reaction sequence, if the entire CO formed in the decomposition reaction (equation 3) is consumed in the water gas shift reaction (equation 4), coincidence in the proportion of products by steam reforming and by decomposition-water gas shift reactions could be expected. The presence of a good amount of CO suggests that the rate of water gas shift (WGS) reaction is not fast over the present catalyst system. This observation together with the data summarized in table 1 suggests the participation of decomposition of methanol during the steam reforming of DME over the Ga_2O_3-Al_2O_3 catalysts. The decomposition-WGS scheme has been proposed by several authors for methanol steam reforming over copper and Pd catalysts [21–23]. During the DME steam reforming over the Ga_2O_3-Al_2O_3 catalysts, the H_2 production is controlled by the rates of direct methanol steam reforming, methanol decomposition and the WGS reaction. Due to the highly endothermic nature of the DME steam reforming reaction, the formation of CO can not be significantly reduced because of the equilibrium [24,25]. Thus the WGS reaction and its relative rate with the other reactions influences the overall H_2 yield in the effluent mixture.

It has to be noted that, below 573 K, an appreciable amount of DME was observed both in the steam reforming and decomposition reactions of methanol (figure 5). This indicates that the hydrolysis of DME is

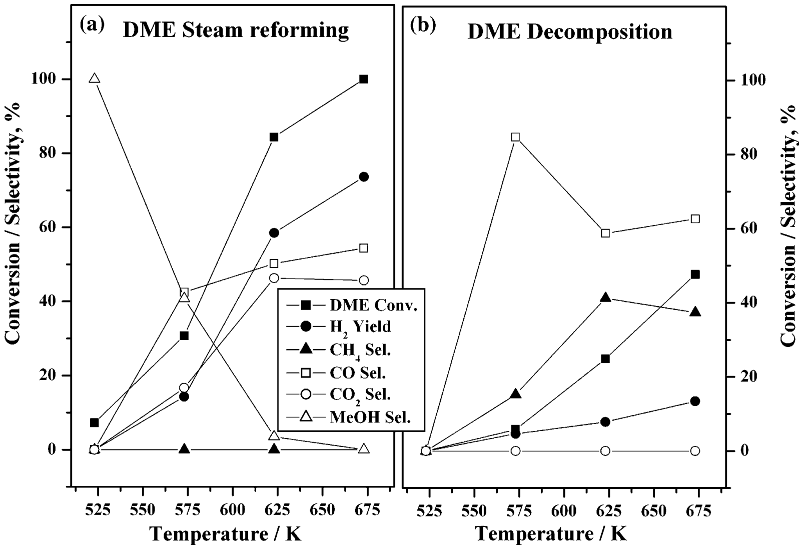

Figure 4. Comparison of DME steam reforming (a) and DME decomposition (b) on $Ga_8Al_2O_{15}$ at 523–673 K. Both steam reforming and decomposition reactions were at a gas hourly space velocity of 20000 h^{-1}.

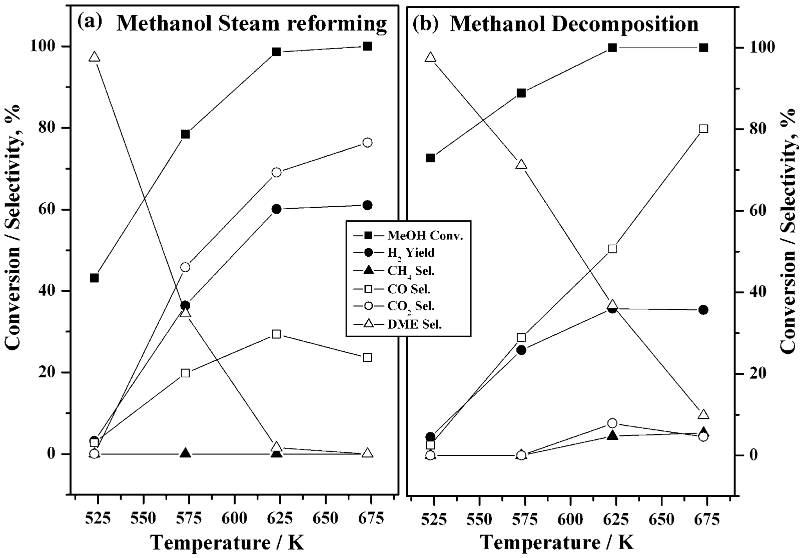

Figure 5. Comparison of methanol steam reforming (a) and methanol decomposition (b) on $Ga_8Al_2O_{15}$ at 523–673 K. Both steam reforming and decomposition reactions were at a gas hourly space velocity of 20000 h^{-1}.

under the equilibrium and a temperature of $T \geq 573$ K is required to disturb the equilibrium as reported in the literature [16]. Thus, it is considered that a higher reaction temperature is required for the H_2 production with the steam reforming of DME, than with the steam reforming methanol. This is further substantiated by comparing the steam reforming reactions of DME and methanol over the $Ga_8Al_2O_{15}$ catalyst. It was found that the DME steam reforming reaction requires a high temperature of 623–673 K for the 100% DME conversion (figure 4a). On the other hand, the methanol steam reforming over the same catalyst exhibited a comparatively high conversion with good reforming activity even at a low temperature of 573 K (figure 5a). Since the reforming reaction of DME is accomplished *via* methanol steam reforming, the equilibrium reaction of the DME hydrolysis makes the difference in the activity. The above results indicating that the hydrolysis of DME is the rate limiting step for the DME steam reforming reaction over the present catalyst system. A similar reaction mechanism has been reported for Cu-loaded catalysts [16]. Over Ga_2O_3–Al_2O_3, the hydrolysis of DME could be taken place to a greater extent on the active species of Ga_2O_3. This will effectively reduce the number of active species available for the steam reforming reaction. Thus, it is possible that a comparatively high temperature is required for the Ga_2O_3 catalysts to achieve the complete conversion of DME to CO_x and H_2.

Although $Ga_xAl_{10-x}O_{15}$ is active for DME steam reforming, a comparatively high temperature is needed for good catalytic performance with respect to the Cu-loaded samples [16]. In the case of Cu-loaded catalysts, the high methanol reforming activity of Cu is very much helpful for disturbing the equilibrium for DME hydrolysis and thereby enhances the DME conversion. To substantiate this, DME steam reforming reaction was carried out on selected compositions of Cu (10 mol%)/$Ga_xAl_{10-x}O_{15}$ and presented in table 2. As evident from the data, approximately 90–100% conversion of DME and H_2 yield could be achieved only at 673 K for $Ga_xAl_{10-x}O_{15}$ at $x \geq 4$, whereas the same occurred at the comparatively low temperature of 623 K for Cu/$Ga_xAl_{10-x}O_{15}$ at any value of 'x'. These results indicate that the hydrolysis of DME over Cu loaded samples is promoted by the consumption of methanol with steam reforming over copper as reported in the literature [16]. Thus, the DME conversion reaches 100% at a lower reaction temperature over Cu loaded samples in comparison with the Ga_2O_3–Al_2O_3 mixed oxides.

3.2. Characterization

The XRD patterns of $Ga_xAl_{10-x}O_{15}$ showed two broad peaks approximately at $2\theta = 33°$ and 63° indicating that the amorphous character predominates in the material, which probably is due to the preparation method. The peak maximum around 33 ° is slightly shifted to a higher 2θ as the Ga_2O_3 concentration increases. An increase in the peak intensity was observed in proportion to the Ga_2O_3 content. γ-Al_2O_3, γ-Ga_2O_3 and $GaAlO_3$ are the most probable phases under the present preparation conditions of the catalyst [18–20]. However, it is quite difficult to elucidate these phases from the broad peak of the XRD pattern. Figure 6 shows the typical XRD patterns of Al_2O_3, Ga_2O_3 and selected compositions of the Ga_2O_3–Al_2O_3 mixed oxides. The BET surface areas of the simple oxides and Ga_2O_3-Al_2O_3 mixed oxides are listed in table 1. An increase in the surface area was observed from Al_2O_3 when a small amount of Ga_2O_3 is added to it. However, the effect of improvement in the surface area is clearly pronounced when Al_2O_3 is added to Ga_2O_3. The addition of a small amount of Ga_2O_3 to alumina (and vice versa) probably modifies the pore structure during the mixed oxide formation and results in an increase in surface area as previously reported [18–20]. However, no obvious correlation was observed between the surface area and composition among the mixed oxides. In the NH_3-TPD measurements for $Ga_xAl_{10-x}O_{15}$, a single broad desorption peak was observed between 323 K and 493 K for all the compositions without an apparent peak. Complete desorption of NH_3 below 500 K indicates the absence of strong acidic sites of the kind that are often observed in silica-alumina or zeolite materials. The relative acidity value obtained from the NH_3–TPD measurement is included in table 1. Even though surface area and acidity are decisive factors for better catalytic performance, in the present study, no obvious correlation was observed between these two parameters and the activity.

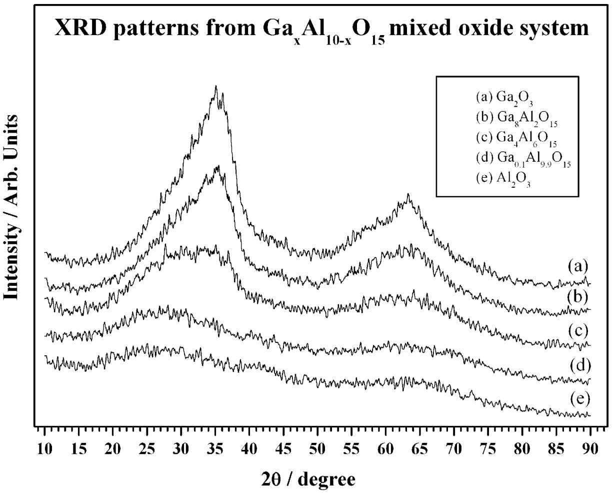

Figure 6. X-ray diffractograms of Al_2O_3, Ga_2O_3 and selected compositions of Ga_2O_3–Al_2O_3 mixed oxides at room temperature after calcination at 773 K.

There has been a growing interest in the use of Ga^{3+} in the catalytic systems [18–20,26–28]. One of these studies revealed that the Ga atoms located at the surface atomic sites (T_d and O_h) of Al_2O_3 and GaO_4 tetrahedra highly dispersed in the surface spinels are responsible for the high activity in the selective reduction of NO by

Table 2
DME steam reforming activity data for Cu-loaded samples

Composition Cu/$Ga_xAl_{10-x}O_{15}$) (10 mol% Cu)	DME Conversion (%)	H_2 Yield (%)	Selectivity/%		
			MeOH	CO_2	CO
Cu/Al_2O_3	99	68	0	99	1
Cu/ $Ga_2Al_8O_{15}$	100	72	0	75	23
Cu/ $Ga_8Al_2O_{15}$	98	82	0	92	8
Cu/Ga_2O_3	99	74	0	93	7

Reaction conditions: 623 K, SV = 20000 h^{-1} mL (g cat)$^{-1}$, Feed gas composition; 1% DME and 3% H_2O diluted with N_2.

propene [27]. The present study clearly shows that the addition of Ga_2O_3 enhances the DME conversion and H_2 yield, but an understanding of the role of Ga_2O_3 is currently unavailable and would require further investigation. Previously, the DME steam reforming catalyst was designed by the combination of an acidic support and the methanol steam reforming catalysts. The interesting aspect of the present study is without using a conventional methanol steam reforming catalyst, the Ga_2O_3–Al_2O_3 mixed oxides and Ga_2O_3 exhibited good performance in the DME steam reforming reaction. Further studies directed towards the exploitation of the system on different aspects are underway and will be reported elsewhere.

4. Conclusions

The present study evidence that the Ga_2O_3–Al_2O_3 mixed oxides and Ga_2O_3 show good activity for the DME steam reforming reaction. The catalysts with higher amounts of Ga_2O_3 leads to higher DME conversion and H_2 yield. The steam reforming of DME over Ga_2O_3 and the Ga_2O_3 containing mixed oxides occurs *via* successive two step reactions of DME hydrolysis and methanol steam reforming. The comparison of steam reforming of DME between $Ga_xAl_{10-x}O_{15}$ and $Cu/Ga_xAl_{10-x}O_{15}$ catalysts reveals that the former required comparatively higher temperature of 623–673 K for achieving high DME conversion and H_2 yield. So far in the literature, an active transition metal component supported on an acidic oxide is used for the reforming reaction. The interesting aspect of the present study is that without an additional transition metal component, Ga_2O_3 and Ga_2O_3 containing Al_2O_3 mixed oxide system exhibited good activity in the reforming reaction.

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