NOVEL MESOPOROUS SILICA INCORPORATED ISOLATED Ti FOR PHOTOCATALYTIC REDUCTION OF CO$_2$ TO CH$_4$

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Abstract
Novel Ti–KIT–6 materials with different Si/Ti ratios (200, 100 and 50) have been synthesized, characterized and applied for the photocatalytic reduction of carbon dioxide to methane. An intermediate amount of Ti (Si/Ti=100) was found to be isolated and uniformly distributed, without collapsing the KIT–6 structure. TiO$_2$ formation was observed due to a higher amount of Ti (Si/Ti=50). Overall, the Ti–KIT–6 (calcined) materials were superior in activity than the Ti–KIT–6 (dried) materials. It was found that methane production was mainly dependent on the superior physical properties, structure connectivity and morphology of the KIT–6 mesoporous materials, which provided better access to adsorb CO$_2$ and H$_2$O to react Owing to the greater number of OH groups, the Si/Ti ratio of 100 showed a higher methane production rate and was found to be more reactive than commercial Degussa P25.

Introduction
Global warming, which is mainly due to the increasing levels of greenhouse gases in the atmosphere, has become a key challenge for the world. Carbon dioxide (CO$_2$), which is mainly obtained from fossil fuel combustion [1], is the main contributor of this situation. The preferable way of reducing CO$_2$ is to recycle it as fuel feedstock, with energy input from cheap and abundant sources [2]. Photocatalytic technology to convert CO$_2$ into fuel has recently attracted the attention of many researchers and has become a promising application. This technology simply uses ultraviolet (UV) and/or visible light as the excitation source for semiconductor catalysts, and the photoexcited electrons reduce CO$_2$ with H$_2$O on the catalyst surface to form energy-bearing products such as carbon monoxide (CO), methane (CH$_4$), methanol (CH$_3$OH), formaldehyde (HCHO), and formic acid (HCOOH). Photocatalysts such as TiO$_2$, CdS, ZrO$_2$, ZnO, and MgO photocatalysts have been investigated, among them wide band-gap TiO$_2$ catalyst (3.2eV) are considered the most convenient candidate in term of cost and stability. [3]. However, the design of highly efficient and selective photocatalytic systems for the reduction of CO$_2$ with H$_2$O is of vital interest [4]. It has been shown that
highly dispersed titanium oxide (Ti–oxide) catalysts anchored on porous Vycor glass, zeolites and some mesoporous silica materials exhibit a high and characteristic photocatalytic reactivity compared to bulk TiO$_2$ powder [5]. However Korea Advanced Institute of Science and Technology–6 (KIT–6) silica is an attractive material with 3–dimensional (gyroid cubic Ia3d) pore structure and large pore size, which has already received attention of many researchers for other applications. An attempt has therefore been made in the present work to prepare highly dispersed isolated Ti–material within the novel KIT–6 mesoporous silica with attractive physical properties, cavities and frameworks in order to utilize them as photocatalysts for the photocatalytic reduction of CO$_2$ with H$_2$O to form CH$_4$.

**Experimental**

KIT–6 mesoporous silica material was synthesized following the procedure reported in [6]. The solid product obtained after the hydrothermal treatment was filtered, dried and calcined at 550 °C for 5h and was then utilized to prepare Ti–KIT–6 (dried or calcined). The dried and calcined KIT–6 materials were then treated with Titanium (IV) isopropanoxide (98 %) at different Si/Ti ratios (200, 100 and 50) and finally calcined to achieve Ti–KIT–6 following the procedure recently reported [7]. Furthermore, photocatalytic activity test was carried out in the basic experimental set-up can be found in our previous work [8]. The set-up includes a Pyrex glass reactor, connectors, mass flow controllers, water bubbler, and a UV lamp (Osram Ultra–Vitalux 300 W). It also has a CO$_2$ gas cylinder (99.99%), a gas chromatograph (Varian CP–3800) equipped with a capillary column (CP7381) and a flame ionization detector (FID). A photocatalytic reaction was performed in the Pyrex glass reactor which contained the photocatalyst. CO$_2$ gas was introduced into the reactor after passing it through the water bubbler. When equilibrium was reached, the UV light was turned on and the reaction products were analyzed by means of the GC. Blank tests were also conducted to ensure that the product was due to the photocatalytic reaction. The blank tests were a UV illumination without the photocatalyst and a reaction in the dark with the catalyst.

**Results and Discussion**

The physical and textural properties obtained by means of N$_2$ sorption of the KIT–6 and Ti–KIT–6 materials are shown in Table 1. A noticeable decrease was observed in the surface area and pore volume of KIT–6 after Ti incorporation with different Si/Ti ratios in both the dried and calcined samples. The surface area and pore volume of the Ti–KIT–6 (dried) materials were slightly higher than those of Ti–KIT–6 (calcined), which might be due to the easy incorporation of Ti in the dried weak structure of KIT–6. However, Ti can be trapped in the bulk of the KIT–6 (dried) material but not in that of the rigid structure of KIT–6 (calcined). The average pore diameter did not change significantly and remained uniform, which might be due to the three–dimensional (3–D) pore structure of KIT–6, which is able to accommodate the Ti dispersion.
Table 1: Physical properties of synthesized Ti–KIT-6 materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$</th>
<th>PV</th>
<th>APD</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ti–KIT–6(Dried) (Si/Ti=200)] Calcined</td>
<td>865</td>
<td>1.11</td>
<td>6.55</td>
</tr>
<tr>
<td>[Ti–KIT–6(Dried) (Si/Ti=100)] Calcined</td>
<td>767</td>
<td>0.80</td>
<td>6.48</td>
</tr>
<tr>
<td>[Ti–KIT–6(Dried) (Si/Ti=50)] Calcined</td>
<td>730</td>
<td>0.67</td>
<td>6.45</td>
</tr>
<tr>
<td>KIT–6 Calcined</td>
<td>772</td>
<td>1.04</td>
<td>6.49</td>
</tr>
<tr>
<td>[Ti–KIT–6(Calcined) (Si/Ti=200)] Calcined</td>
<td>726</td>
<td>0.95</td>
<td>6.45</td>
</tr>
<tr>
<td>[Ti–KIT–6(Calcined) (Si/Ti=100)] Calcined</td>
<td>700</td>
<td>0.85</td>
<td>6.40</td>
</tr>
<tr>
<td>[Ti–KIT–6(Calcined) (Si/Ti=50)] Calcined</td>
<td>684</td>
<td>0.73</td>
<td>6.41</td>
</tr>
</tbody>
</table>

$S_{BET}$ (BET specific surface area in m$^2$/g); PV (cumulative pore volume in cm$^3$/g); APD (average pore diameter in nm)

TEM was performed in order to analyze the mesoporous structure of KIT–6 and dispersion of isolated Ti on the KIT–6 support material. An ordered array of mesopores, which corresponds to the formation of the KIT–6 material, can be observed in Fig. 1 (a). Moreover, the centers of two adjacent pores are about 10 nm apart and the pore diameter is about 6 nm which is in agreement with the APD obtained from the nitrogen sorption analysis shown in Table 1. Fig. 1 (b,c,d) shows the TEM images of Ti–KIT–6 with Si/Ti ratios of 200, 100 and 50, respectively. The Ti–KIT–6 (Si/Ti=200) depicted in Fig. 1 (b) shows a good dispersion of Ti and does not show any agglomeration of the Ti particles; it has preserved the structure of the support as can be confirmed by the KIT–6 mesopore channels. A similar trend can be seen in the case of Ti–KIT–6 (Si/Ti=100), which shows a good Ti dispersion and mesopore structure preservation, as can be observed in Fig. 1 (c). However, in the case of Ti–KIT–6 (Si/Ti=50), the mesopore structure of KIT–6 is partially collapsed/damaged, as can be seen on the right side of Fig. 1 (d); this is due to the higher Ti content than the other two ratios of 200 and 100, and favoured the formation of TiO$_2$ (not shown).

Fig. 2 (a) shows the Ti(2p) XPS spectra for Ti–KIT–6 with different Ti contents, and shows a Ti(2p$_{3/2}$) and Ti(2p$_{1/2}$) doublet with a separation of 5.75 eV [9]. It has been observed that the Ti(2p$_{3/2}$) line was shifted towards a lower binding energy for an increased Ti content for Si/Ti ratios 200 to 50. As can be seen in the deconvoluted XPS spectra in Fig. 2 (b,c), the Ti(2p$_{3/2}$) line shifted even further to 458.0 eV, which is close to the binding energy of Ti(2p$_{3/2}$) of pure TiO$_2$ for an increased Ti loading at Si/Ti=50. A similar trend has been found in the O1s spectra of the Ti–KIT–6 materials, as shown in Fig. 2 (d,e,f), where the O1s line at 533 eV was gradually shifted to lower binding energies for the increased Ti content. The deconvoluted XPS spectra of Ti–KIT–6 at Si/Ti ratios of 100 and 50 showed two peaks at 533 eV for Si–O–Si and 530.8 eV corresponding to Ti–O–Ti, which indicate that there is more free TiO$_2$ phase formation in Ti–KIT–6 (Si/Ti=50) than in Ti–KIT–6 (Si/Ti=100), as can be seen from the TEM analysis.
Figure 1 TEM images of (a) KIT–6, (b) Ti–KIT–6 (Si/Ti=200), (c) Ti–KIT–6 (Si/Ti=100) and (d) Ti–KIT–6 (Si/Ti=50), showing the KIT–6 material structure preservation/damage due to Ti distribution.

Figure 2. XPS analysis of Ti–KIT–6 materials showing the difference in (a) Ti2p overall, and (b,c) deconvolution of Ti–KIT–6 (Si/Ti=100,50 ratios), (d) O1s overall, and (e,f) deconvolution of Ti–KIT–6 (Si/Ti=100,50 ratios).

Blank tests conducted in the absence of photocatalysts as well as the reaction in the dark with catalysts, showed no product formation. CH₄ was the main product detected in all the reaction experiments. Fig. 3 (a,b) shows the production rate of the CH₄ formation that originated because of the unique properties of the charge...
transfer excited state, i.e., \((Ti^{3+}−O^{−})^*\) of the tetrahedrally-coordinated titanium oxide species within the silica frameworks [10]. It can be seen that Ti–KIT–6 (calcined or dried)(Si/Ti=100) show higher activity than the Si/Ti ratios of 200 or 50. This is due to the combined contribution of the high dispersion state of the Ti–oxide species, which is caused by the large pore size with a 3D channel structure and the lower formation of Ti–O–Ti or TiO₂ agglomerates, as was confirmed by TEM and XPS analysis. In addition, Fig. 3 (c) shows a high CH₄ production for Ti–KIT–6 (Si/Ti=100) with more concentrations of OH groups which actually affect the adsorption properties of the water on the catalyst surface [10]. The ratio between H₂O and CO₂ is another parameter that determines the selectivity of CH₄ or CH₃OH. When H₂O/CO₂ is high, the selectivity for CH₄ formation becomes higher. On the basis of the Ti shown in Fig. 3 (d), it can be stated that the above mentioned optimized photocatalyst showed better activity than the best commercial TiO₂ (Degussa P25).

Figure 3. Methane formation comparison by photocatalytic reduction of carbon dioxide and water (a) Ti–KIT–6 (dried)(Si/Ti=200,100,50 ratios), (b) Ti–KIT–6 (calcined)(Si/Ti=200,100,50 ratios), (c) effect of OH groups on activity and (d) activity comparison on Ti basis with commercial Degussa P25.

Conclusion
Novel synthesized Ti–KIT–6 materials with different Si/Ti ratios (200, 100 and 50) have revealed that Ti–KIT–6 (Si/Ti=100) showed higher CH₄ formation than Ti–KIT–6 (Si/Ti=200, 50). The high activity of the optimized photocatalyst was found to be due to the lower number of Ti–O–Ti or TiO₂ agglomerates and the more isolated Ti species that were uniformly dispersed on the KIT–6 mesoporous silica support without damaging the mesopore structure. The increase in OH groups found in Ti–KIT–6 also favoured higher activity. The activity of the
optimized Ti–KIT–6 (Si/Ti=100) was also much higher than the commercial Degussa P25 TiO₂. Novel KIT–6 containing highly dispersed isolated Ti species is a promising and effective photocatalyst candidate for the reduction of CO₂ to CH₄ and indicates that it is suitable for further optimization.

Acknowledgments
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References