Effective Synthesis of \textit{m}-Xylylene Dicarbamate via Carbonylation of \textit{m}-Xylylene Diamine with Ethyl Carbamate over Hierarchical TS-1 Catalysts

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ABSTRACT: Carbonylation of \textit{m}-xylylene diamine (XDA) with ethyl carbamate to produce \textit{m}-xylylene dicarbamate (XDC), which is the crucial intermediate for the production of \textit{m}-xylylene diisocyanate (XDI), over the hierarchical TS-1 (HTS-1) zeolite catalyst was studied. The catalysts were characterized by Brunauer–Emmett–Teller, X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and temperature-programed desorption of ammonia techniques systematically. The results showed that the high performance of HTS-1 could be attributed to the weak acidity and high $V_{\text{meso}}/V_{\text{total}}$ ratio of the catalyst. Impacts of reaction time and reusage on the HTS-1 catalyst were also investigated. Under 6 h and 200 °C, XDA conversion could reach 100% with 88.5% XDC yield. Furthermore, partial loss of Ti active sites with Lewis acidity on the catalyst surface led to the decrease of XDC yield during recycling. Moreover, a possible reaction mechanism for the title reaction was primarily proposed.

1. INTRODUCTION

\textit{m}-Xylylene diisocyanate (XDI) is a kind of aliphatic isocyanate with the structure of the $\text{CH}_2$ group between the benzene ring and isocyanate group. This structure makes it resistant to yellowing, thus being applied in the field of high-grade coatings, medical polyurethane, and so forth. Furthermore, because of the similar refractive index between human eyes and resin flakes made from XDI-based polyurethanes, it is widely used in the field of high-grade polyurethane glasses.\textsuperscript{1,2}

Industrially, isocyanate is produced via the carbonylation of phosgene with \textit{m}-xylylene diamine (XDA).\textsuperscript{3,4} which has the disadvantages of extreme toxicity and the formation of corrosive HCl. Among various phosgene-free methods, thermal decomposition of carbamate is considered as the most effective way, which generally contains two consecutive processes: (1) first, the synthesis of the intermediate of carbamate as the precursor for thermal decomposition and (2) subsequently, the thermal decomposition of carbamate to isocyanate with the depletion of alcohol during the reaction.\textsuperscript{5,6} Therefore, the synthesis of carbamate is very important for the production of isocyanate via a phosgene-free route.

Traditionally, carbamates were synthesized by alcoholysis of substituted ureas, oxidative carbonylation of amines, and reductive carbonylation of nitro-compounds. However, these routes suffered from high temperature, high cost of the noble catalyst, or high risk in safety.\textsuperscript{7} In order to overcome the aforementioned problems, the carbonylation of diamines with low-molecular-weight carbamates has become an attractive route in recent years. On account of these reasons, an efficient synthesis route for \textit{m}-xylylene dicarbamate (XDC) from the reaction of XDA with ethyl carbamate (EC) was developed, as shown in Scheme 1. Because EC could be readily synthesized

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via alcoholsysis of urea, this route also can be considered as 
CO2 indirect utilization, in the process of which CO2 was 
deemed as the original carbonylation reagent in the whole 
chains.8 It should be noted in the previous results that the 
efficiency of the reaction is limited without an effective catalyst. 
This issue is expected to be overcome by the involvement of a 
proper catalyst.

Over the past few years, carbamate syntheses over several 
homogeneous and heterogeneous catalysts have been reported, 
such as Mg,Zr,Al-MMO,11 Ga,O,12 Mg-Al-Y,13 Cu-
CPO-27,14 alkali-treated zeolites,15 Ce-Zn,16 tungstophos-
phoric acid (TPA/K30),17 Mn(OAc)2,18 Pd/ZrO2,19 
NaOCH,20 CuCl/ionic liquids,21 [BSO,HMIm][OTf],22 
Se,23 AlSBA-15,24 Zn/SiO,25 and 3-amino-1,2,4-triazole 
potassium (KATrizz).26 However, difficulties in homogeneous 
catalyst separation and low catalytic activity for the 
heterogeneous catalysts resulted in difficulties in the scale-up 
process. Therefore, an effective heterogeneous catalyst is still 
highly desired.7

Titanium silicate (TS-1) zeolite possesses the properties of 
high total surface area, thermal stability, low toxicity, 
reusability, ion exchange capability, and easy handling. 
Therefore, it is widely applied in the reaction of oxidation, 
epoxidation, alkylation, acylation, and cyclic condensa-
tion.27,35 However, the particle size of traditional TS-1 
nanoparticles is usually small, thus resulting in limitations of 
intracrystalline diffusion.

Hierarchically porous zeolites, especially hierarchical TS-1 
(HTS-1) zeolites with a MFI topological structure, have 
received great attention in catalytic oxidation processes 
because of their microporous and mesoporous/macroporous 
characteristics which enhance the mass transport and improve 
catalytic performance. Srivastava et al. used titanium silicate 
to catalyze the formation of carbamates using CO2 as the raw 
materials, and it showed good results.36 Therefore, the 
application of the HTS-1 catalyst in XDC production is of 
great significance.

Herein, we report an efficient and environment-friendly 
route for the synthesis of XDC. In this work, HTS-1 catalysts 
with different Ti contents were prepared by the hydrothermal 
method and then used in the carbonylation of XDA to XDC 
for the first time. The physicochemical properties of the 
catalysts were characterized by the Brunauer–Emmett–Teller 
(BET) method, X-ray diffraction (XRD), Fourier transform 
infrared (FT-IR) spectroscopy, scanning electron microscopy 
(SEM), and temperature-programed desorption of ammonia 
(NH3-TPD). The effects of reaction time on the catalytic 
performance, as well as the reuse of the HTS-1 catalyst, were 
studied. Furthermore, the reaction mechanism was studied.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Hierarchically Porous HTS-1 Cata-

ysts [TS-1-(0), TS-1-(1), TS-1-(2), and TS-1-(3)]. Tetrabu-

tyltitanate was mixed with tetraethylorthosilicate with the 
molar ratio of the composition being 100SiO2/nTiO2 (n = 0, 
1.19, 2.38, and 3.57) at 0 °C for 3 h under stirring, followed by 
addition of tetrapropylammonium hydroxide (TPAOH) (25% 
wt) with the molar ratio of the composition being 100SiO2/ 
30TPAOH/124H2O at 0 °C for 12 h under stirring. The as-
obtained mixture was crystalized at 180 °C for 2 days. The 
sample was washed with distilled water and dried overnight 
at 80 °C, followed by calcination at 550 °C for 6 h. Then, the 
resulting products were named TS-1-(0), TS-1-(1), TS-1-(2), 
and TS-1-(3), respectively.

2.2. Characterizations. Powder XRD patterns were 
recorded using a Bruker D8 ADVANCE X-ray diffractometer with CuKa radiation (k = 0.15406 nm) over a 2θ range of 5–
90°. The working voltage and applied currents were 40 kV and 
40 mA, respectively. SEM images of the samples were obtained 
using Bruker Nova NanoSEM operated at 5.0 kV. Nitrogen 
adsorption–desorption isotherms were measured at 77 K using 
a Micromeritics ASAP 2020 M instrument, and the sample was 
outgassed at 300 °C for 10 h prior to measurement.

N2-physisorption was carried out at 77 K by using an 
adsortion apparatus (ASAP 2460). Before the analysis, the 
samples were evacuated at 200 °C for 4 h in vacuum. The 
specific surface area (SBET) was determined by the BET 
equation. The total pore volume (Vpore) was obtained based on 
the stored nitrogen volume when the relative pressure was 
0.99. The S Nico, S Nano, V Nico, and V Nano were calculated by the 
t-plot method. The element contents were analyzed with 
inductively coupled plasma emission spectroscopy (ICP, 
Varian 710-ES) after the sample was solved. The FT-IR 
spectra of the catalysts were collected using a Nicolet NEXUS 
670 FT-IR spectrometer, and the sample to be measured was 
ground with KBr and pressed into thin wafers.

The yield of the product in the sample was calculated 
through the data obtained by gas chromatography. The 
conversion of XDA and selectivity of XDC were calculated as 
follows

\[ \text{Conv. (XDA)} \%= \frac{n_{\text{f}}(\text{XDA}) - n_{0}(\text{XDA})}{n_{0}(\text{XDA})} \times 100\% \] (1)

\[ \text{Sel. (XDC)} \%= \frac{n(\text{XDC})}{n_{0}(\text{XDA}) - n(\text{XDA})} \times 100\% \] (2)

where n0(XDA) is the molar amount of XDA added before 
the reaction, n(XDA) is the molar amount of XDA remaining 
after the reaction, and n(XDC) is the molar amount of the target 
product produced by the reaction.

In this paper, in order to facilitate the evaluation of catalyst 
conversion efficiency, the value is defined as the amount of 
XDC (mmol) converted per hour per titanium content (mole), 
and the unit of this value is mmol XDC·mol Ti·h⁻¹, and the 
calculation formula is as follows

\[ \text{catalyst activity} = \frac{n(\text{XDC})}{n_{\text{Ti}} \times t} \times 1000 \] (3)
where $n_{\text{XDC}}$ is the amount of XDC produced by the reaction (mol), $n_{\text{Ti}}$ is the titanium content of the catalyst added to the reaction system (mol), and $t_r$ is the reaction time (h).

### 2.3. Catalytic Reaction and Recyclability

All reactions were conducted in a 100 mL stainless-steel autoclave equipped with a magnetic stirrer. Approximately 1.36 g (0.01 mol) of XDA, 4.45 g (0.07 mol) of EC, and 0.2 g of [14.7 wt % (based on XDA)] the catalyst were charged successively into a round-bottomed flask and reacted at 463–483 K with stirring for 1–8 h. After the reaction, the flask was cooled down to room temperature. About 50 mL of methanol was added to dissolve XDA, XDC, and other byproducts. The insoluble byproducts were removed by filtration or centrifugation if needed.

### 3. RESULTS AND DISCUSSION

The surface areas and pore volumes of HTS-1 samples with different loadings are presented in Table 1. The as-prepared HTS-1 catalysts were found to have a relatively large surface area (398–419 m$^2$/g) and total volume (0.213–0.265 cm$^3$/g), which was expected to expose abundant active sites. Note-worthy to say, abundant mesopores in the HTS-1 were formed during catalyst preparation. According to the calculation result, the ratios of the mesopore volume to total volume ($V_{\text{meso}}/V_{\text{total}}$) of these samples are all higher than 20%, suggesting the hierarchical structure of these TS-1 catalysts.

Catalyst acidities of various TS catalysts were measured by NH$_3$-TPD. In the previous report, the ethoxy carbonylation of diamine was proven to be an acid catalytic reaction, and an acidic catalyst can promote this reaction efficiently. It is generally accepted that two kinds of acid sites exited on the surface of TS-1 zeolites, namely, the weak acid site and the strong acid site. The catalytic reactions were found to be highly dependent on the acid site strength in different temperature ranges.
strong acid site, which originated from the framework Ti(IV) ions and the silanol groups at crystal defects, respectively.\textsuperscript{37}

\(\text{NH}_3\)-TPD profiles for HTS-1 catalysts in Figure 1 showed two major desorption zones approximately at 130–140 °C for weak acidic sites and 285–345 °C for strong acid sites. All the HTS-1 catalysts clearly exhibited major weak acidic sites and a small proportion of strong acidic sites. The weak acidity increased for various HTS-1 catalysts in the sequence TS-1-(1) < TS-1-(2) < TS-1-(3), which was well consistent with the trends of XDC yields (Table 2), suggesting that the role of weak acidity of HTS-1 is significant in the catalytic performance. Meanwhile, the bare MFI without Ti loading [TS-1-(0)] exhibited slightly weak acidity. Figure 2 displays the XRD patterns of HTS-1 catalysts. All of these samples exhibited typical diffraction peaks at 2\(\theta\) = 7.8, 8.8, 23.2, 23.8, and 24.3°, which are coincident with the MFI zeolitic topology.

Then, FT-IR analysis was carried out for the HTS-1 samples, and the result in Figure 3 shows that the framework of the strong acid site, which originated from the framework Ti(IV) ions and the silanol groups at crystal defects, respectively.\textsuperscript{37}

Figure 1. SEM images of TS-1-(1) (a,b); TS-1-(2) (c,d); TS-1-(3) (e,f).

Figure 2. XRD patterns of TS-1-(3) and deactivated TS-1-(3).

Figure 4. SEM images of TS-1-(1) (a,b); TS-1-(2) (c,d); TS-1-(3) (e,f).

Figure 5. Recycling graph for TS-1-(3) for the synthesis of XDC.

Figure 6. XRD patterns of TS-1-(3) and deactivated TS-1-(3).
zeolite was retained by the evidence of characteristic peaks of internal vibrations of (Si, Ti)O₄ (1100 and 800 cm⁻¹), double-ring tetrahedral vibrations (1230 cm⁻¹), and asymmetric stretching of SiO₂ and TiO₂ tetrahedra (550 cm⁻¹). What is more, compared with TS-1(0), because of the incorporation of Ti ions, TS-1(1), TS-1(2), and TS-1(3) all showed the absorption peak of Si–O–Ti at 960 cm⁻¹ and increased in intensity with increasing Ti content. This is because of the overlap of the Si−(OH) stretching mode of the silanol groups of silica with the Si−O–Ti asymmetric stretching mode involving Ti dissolved into the silica framework. Figure 4 shows the SEM images of HTS-1 stretching mode involving Ti dissolved into the silica−because of the overlap of the Si–O–Ti at 960 cm⁻¹ and increased in intensity with increasing Ti content. This is because of the overlap of the Si−(OH) stretching mode of the silanol groups of silica with the Si−O–Ti asymmetric stretching mode involving Ti dissolved into the silica framework.88 Figure 4 shows the SEM images of HTS-1 samples synthesized with different Ti loading levels. The results showed that different from the reported smooth surface of traditionally prepared microporous TS-1, all the HTS-1 samples with a mean size of around 1.5 μm showed uniform particles with a rough surface and layered structure, which is the characteristic morphology of the HTS-1 catalyst.

The effects of the various hierarchical TS catalysts with varying Ti loadings on the ethoxy carbonylation of XDA with EC were further tested. First, when a blank reaction was carried out without any catalyst, only a 26.4% XDC yield was obtained. After adding pure MFI without Ti species, the XDC yield sharply increased to 56.6%, whereas the bare MFI without Ti loading [TS-1-(0)] possessed slightly weak acidity but exhibited a relatively higher XDC yield in comparison with the blank result without any catalyst, which might be attributed to the influence of its higher strong acidity derived from Si–OH groups. However, the XDC yield also decreased to 51.3% for TS-1-(1) after introduction of a small amount of Ti, that is, 0.85%. It should be noted that pure MFI exhibits a Vₘₑₒₛ/Vₜₜₒₜₜ ratio of 0.357[TS-1-(0)], while the TS-1-(1) catalyst showed an obviously lower Vₘₑₒₛ/Vₚₜₜ ratio of 0.296 after introduction of 0.85 wt% Ti. With a further increase of Ti from 0.85% in TS-1-(1) to 1.90% in TS-1-(3), the Vₘₑₒₛ/Vₚₜₜ increased from 0.296 to 0.416, and a higher XDC yield of 61.3% was obtained over TS-1-(3). This indicated that XDC yield has a positive correlation with the Vₘₑₒₛ/Vₚₜₜ ratio, indicating that a higher proportion of mesopore volume facilitated the reaction.54 On account of these reasons, the optimum catalyst is TS-1-(3) with a Ti content of 1.90%.

The catalyst TS-1-(3) was used to catalyze the reaction of XDA with EC at a temperature of 200 °C. The results in Table 2 show that the yield of XDC increased from 61.3 to 88.5% upon increasing the time from 1 to 6 h. The reusability of heterogeneous catalysts is an important parameter for practical applications. Therefore, the recyclability of the TS-1-(3) catalyst was tested and the results are shown in Figure 5. The reaction for the synthesis of XDC was carried out under conditions of 200 °C reaction temperature, 6 h reaction time, 14.7 wt% catalyst, and a molar ratio of XDA/EC = 1:7. The catalyst was recycled five times by centrifugation and then directly used in the next run. It can be seen that XDA conversion remained at 100%. In contrast, the XDC yield decreased obviously in the second and third runs and then decreased slightly in the fourth and fifth runs. The ICP spectroscopy results showed that after recycling for five runs, the Ti content decreased from 1.90 to 1.71%. Moreover, compared with the fresh catalyst, the used catalyst did not show any change in the XRD pattern (Figure 6). These results indicate that the structure of the catalyst is maintained after being used five times, and the decrease in the performance of the HTS-1 catalyst was probably on account of the loss of Ti active sites with Lewis acidity on the catalyst surface during recyclability. This finding could provide helpful information for further improvement of the catalysts to meet the requirement of the practical application.

For the carbonylation reaction of a diamine with carbamates, two possible mechanisms have been proposed in the previous literature, that is, the transesterification pathway and alcoholysis pathway. Deng et al. used quasi-in-situ FT-IR spectroscopy to investigate the reaction pathway and verified the formation of substituted urea as the key intermediate,6 while the previous work of our group also gave the experimental evidence for further identification of the alcoholysis reaction mechanism of the carbonylation reaction.7 What is more, no xylene monocarbamate intermediate was detected after the ethoxy carbonylation of XDA with EC by GC in this reaction. Therefore, the reaction mechanism is also considered as an alcoholysis pathway, as shown in Figure 7. The first is the formation of the urea intermediate with the removal of an alcohol molecule, followed by the formation of N-substituted carbamate in the second step with the contemporary elimination of an ammonia molecule. Generally, the amino group of XDA attacks the carbon in the carbonyl group of EC and (3-ureidomethyl-benzyl)-urea (XDU) is generated by

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**Figure 7.** Proposed reaction mechanism for the reaction of XDA, EC, and ethanol over the HTS-1 catalyst.
delivering the ethoxy group. Finally, ethanol attacks the amino group of XDU to form XDC.

4. CONCLUSIONS

In this work, HTS-1 catalysts with different Ti contents were produced via the hydrothermal method and used in the carboxylation of XDA to XDC for the first time. The physicochemical properties of the catalyst were characterized by different techniques, and it turned out that the catalyst exhibited a large external surface area with abundant mesoporous structures. The effects of reaction time on catalytic performance and reusability of the HTS-1 catalyst were studied. Among the catalysts tested, TS-1-(3) with a higher Ti content demonstrated better catalytic activity, and 100% XDA conversion with 88.5% XDC yield was achieved. Furthermore, the reaction mechanism was proposed as an alcoholysis pathway in which the urea intermediate was formed first, followed by the formation of N-substituted carbamate.

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**Notes**

The authors declare no competing financial interest.

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