

CHAPTER VI
CATALYTIC ACTIVITY OF STYRENE OXIDATION OVER Cr-MCM-48
AND Ce-MCM-48

6.1 Abstract

Chromium and cerium incorporated onto MCM-48 were studied their catalytic activities. Chromium species is known to be a good oxidizing material while cerium species is commonly used in three way catalytic converter to oxidize hydrocarbon. Thus, in this work, chromium/cerium containing MCM-48 materials, directly synthesized from silatrane and chromium/cerium nitrate via sol-gel process, were employed to study catalytic activity on styrene oxidation reaction for comparison. It was found that the rate of the reaction and the catalytic behavior of Cr-MCM-48 relied on the reaction temperature, the amount of reactants, and the quantity of the chromium loading. The rate equation according to a two-stage mechanism with a steady state assumption was proposed to be a representative for this reaction. In the case of Ce-MCM-48, the activity was much lower than that of Cr-MCM-48.

(**Keywords:** Cr-MCM-48, Ce-MCM-48, Styrene oxidation reaction, Kinetic study, Two-stage mechanism)

6.2 Introduction

MCM-48, also a member of M41S family [1-2], has three-dimensional pore network, giving less limitation for incoming reactants [3]. Incorporation of transition metals to MCM-48 is also widely used for oxidation reactions of hydrocarbons [4-5]. Outstanding properties of MCM-48 combined with the redox properties of metal loading like chromium seem to be a good promising catalyst. It is also stated elsewhere [6-7] that using hydrogen peroxide (H_2O_2) as a clean oxidant is favored owing to the by-product of water. Many researchers have therefore put effort to achieve MCM-48 based catalysts [8], for instance, our previous work reported a successful synthesis and structural properties of high specific surface area Cr/Ce-MCM-48 via sol-gel process [9].

Zhang *et al.* [10] obtained only 9.7% styrene conversion using Cr-MCM-41 as catalyst. The reaction was performed at 60 °C for 24 h using TBHP as an oxidant. They also found the leach out of chromium species from the color change of the catalyst from orange to white. Among several metals studied they stated that Mn-MCM-41 was the effective heterogeneous catalyst for this reaction. Gómez *et al.* [4] synthesized Cr-MCM-48 using ion exchange and tested the activity on the styrene oxidation. They found that 68% styrene conversion was obtained after 24 h reaction time at 60 °C, and benzaldehyde was the major product. Liu and coworkers [11] studied the synthesis and characterization of Cr-MSU-1 and applied for the same reaction. They revealed that the catalytic performances were strongly affected by the reaction conditions, viz. solvent, styrene/ H_2O_2 ratio, reaction time and temperature. Bai and coworkers [12] synthesized and characterized Cr-containing silica gel by sol-gel method at room temperature. They also tested their catalytic activity via the oxidation of styrene, and found that the synthesized catalyst provided a highly activity without any leaching.

Unlike Cr-MCM-48, a few information of the oxidation of styrene using Ce catalyst was found. Wangcheng *et al.* [13] doped Ln and Ce into the MCM-41 and tested their catalytic behaviors via the oxidation of styrene. The results showed that the Ln-MCM-41 provided the higher reactivity than Ce-MCM-41. They also

indicated that the nature of the metal used led to the differences in the reaction activity.

In this work, we expanded our previous work by studying catalytic properties of Cr/Ce-MCM-48 and the kinetics of Cr-MCM-48 toward the oxidation of styrene using H_2O_2 as the oxidant. The % conversion and products selectivity of this reaction were determined. A suitable mechanism was proposed and investigated using the reaction rate as a function of reactant concentration. The reaction parameters, viz. reaction temperature, ratio of H_2O_2 /styrene, and the amount of metal loading, were also carried out.

6.3 Experimental

6.3.1 Materials

Fumed silica (SiO_2 , 99.8%, Sigma-Aldrich, USA), ethyleneglycol (EG, J.T. Baker, USA), acetonitrile (Labscan, Thailand), sodium hydroxide (NaOH, Labscan, Asia), cetyltrimethylammoniumbromide (CTAB, Sigma-Aldrich, Denmark), chromium(III)nitrate nonahydrate (Himedia, India), and cerium(IV) hydroxide (Sigma-Aldrich, U.S.A.)

6.3.2 Catalyst Preparation and Characterization

Cr-MCM-48 and Ce-MCM-48 were prepared following the procedure described in previous work [9]. The mixture of water, 2M NaOH and CTAB was stirred continuously with slight heating to dissolve CTAB before adding our homemade silatrane into the mixture, followed by adding a required amount of 0.3 M chromium nitrate solution. The mixture was stirred for 1 h. The final molar composition of the gel was $1.0 \text{ SiO}_2:0.3\text{CTAB}:0.50\text{NaOH}:62.0\text{H}_2\text{O}:x\text{Cr}$, where $x = 0.005$ and 0.01 . For Ce-MCM-48 catalysts, a desired amount of cerium glycolate, prepared from cerium hydroxide and EG, was added into mixture with a molar composition of the gel was $1.0\text{SiO}_2:0.3\text{CTAB}:0.50\text{NaOH}:62.0\text{H}_2\text{O}:y\text{Ce}$, where $y = 0.01-0.07$. The resulting mixture was transferred to a Teflon-lined stainless steel autoclave and treated at $140\text{ }^\circ\text{C}$ for 16 h to give solid products which were filtered and dried overnight at ambient conditions. Removal of all organics was performed by

calcination at 550 °C for 6 h (Carbolite, CFS 1200, Hope Valley, U.K.) at a heating rate of 0.5 °C/min. The obtained materials were characterized using a Field emission scanning electron microscope (FE-SEM, Hitachi/S-4800) to achieve the morphology. The order of mesopores was studied using a Transmission electron microscope (TEM, JEOL 2010F).

6.3.3 Catalytic Activity

The oxidation of styrene was introduced to study catalytic activity of Cr/Ce-MCM-48 catalysts. Only Cr-MCM-48 was kinetically studied. Thus, the reaction mixture, composed of 2.5–10 mmol of styrene, a desired amount of 30% H₂O₂, 20ml of acetonitrile, and 0.05g of Cr-MCM-48 catalyst, was stirred in a round bottom flask. The reaction mixtures were sampled at certain time interval then the solid catalyst was filtered. In the case of Ce-MCM-48, the reaction mixture contained 5 mmol of styrene, 5 mmol of 30% H₂O₂, 5 ml of acetonitrile, and 0.05–0.1g of catalyst. The reaction was quenched after 6h and then the solid catalyst was filtered. The products were analyzed on a gas chromatography (GC, Agilent) equipped with a capillary column (ZB-Wax, 0.25mm I.D., 30m) and FID detector. The conversion of styrene was calculated based on the amount of styrene monomer consumed using an internal standard method.

6.4 Results and Discussion

The SEM images (Fig. 6.1) of Cr-MCM-48 with Cr/Si ratios of 0.005 and 0.01, denoted as Cr-MCM-48-0.005 and Cr-MCM-48-0.01, illustrate the edge-truncated octahedral shape, consistent with our previous studies [9]. Unlike Cr-MCM-48 samples, the SEM images of Ce-MCM-48 with all Ce/Si ratios, as shown in Fig. 6.2, illustrate the aggregated of truncated octahedral shape consistent with our previous work [9] and similar to the MCM-48 parent material. The uniform pore channel structure with the incident along [100] was observed using TEM, as seen in Fig. 6.3 and 6.4. It was found that both Cr/Si ratios of 0.005 and 0.01 did not destroy the structure of silica support. These results are also in harmony with our previous

work [9]. On the other hand, the highly ordered pore structure of Ce-MCM-48 materials with all Ce/Si ratios was observed.

Cr-MCM-48 catalysts with different amounts of metal loading were introduced to the oxidation reaction of styrene using hydrogen peroxide as an oxidant. The catalytic activities of these materials were determined in term of styrene concentration as a function of time. The main products obtained were only benzaldehyde and styrene oxide, were reported as % selectivity, as shown in the Table 6.1.

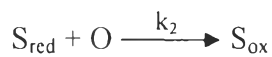
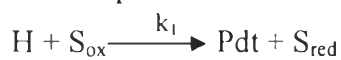
Only Cr-MCM-48-0.005 and Cr-MCM-48-0.01 catalysts were chosen to study the kinetics since both catalysts well maintained the MCM-48 structure, as seen in SEM and TEM. The kinetic study was carried out by varying the reaction temperature of 40°–80 °C. The effect of the temperature on the styrene conversion is shown in Fig. 6.4. It was found that not only the initial rates but also the % conversion of both catalysts, as summarized in Table 6.1, were increased as increasing the temperature, in agreement with the work studied by Saxena *et al.* [14]. When the reaction temperature was adjusted from 40° to 80 °C, % conversion increased from 13.7 to 59.4% and 21.9 to 57.2% for Cr-MCM-48-0.005 and Cr-MCM-48-0.01, respectively. It is worth noting that at 80 °C, the mixture without catalyst provides less than 10% styrene conversion. As a result, the reaction temperature was set at 80 °C for further study.

The effect of the H₂O₂ oxidant quantity on the styrene conversion was also investigated, as can be seen the results in Fig. 6.5. The styrene concentration dramatically decreased with increasing the oxidant amount. Moreover, Table 6.1 shows a significant increase of the % styrene conversion from 28.9 to 94.3% and 31.4 to 91.9% for Cr-MCM-48-0.005 and Cr-MCM-48-0.01, respectively, with increasing the H₂O₂/styrene ratio. The % selectivity of benzaldehyde slightly increased while that of styrene oxide decreased. It could be suggested that too high H₂O₂ concentration led to the C=C bond cleavage to benzaldehyde, giving similar trend to those found by Liu *et al.* [11] who studied the effect of H₂O₂/styrene ratio using Cr-MSU-1 catalyst through the same reaction and observed that the % styrene conversion increased with the ratio. Considering both of our catalysts, it was found

from Table 6.1 that the initial rate of Cr-MCM-48-0.01 was higher than that of Cr-MCM-48-0.005. This might be resulted from having more active sites in Cr-MCM-48-0.01 than the other. The %selectivity of benzaldehyde obtained from using Cr-MCM-48-0.01 catalyst was higher in all cases.

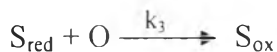
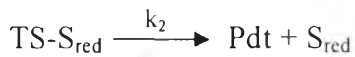
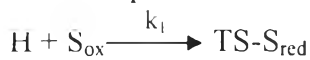
To obtain the rate equation suitable for this study, we applied the equations studied by Saxena *et al.* [14]. The rate constants were solved by means of the least squares method using the observed initial rates and the concentration of the reactants. They proposed two possible mechanisms of the reaction as the redox type and used steady state assumption. Those mechanisms were; two-step and three-step mechanisms [14]. The rate equations were based on adsorption, surface reaction, and desorption of the products, as shown below [14];

Two-step mechanism:



$$\text{Rate} = k_1 k_2 P_H P_O / (k_2 P_O + k_1 P_H)$$

Three-step mechanism:



$$\text{Rate} = k_1 k_2 k_3 P_H P_O / (k_2 k_3 P_O + k_1 k_3 P_H P_O + k_1 k_2 P_H)$$

where H = styrene, O = hydrogen peroxide, Pdt = benzaldehyde and styrene oxide
 S_{ox} = oxidized surface, S_{red} = reduced surface, TS = transition state
(k_1 , k_2 , k_3 are the rate constants in the redox model, and P_H , P_O are the concentrations of styrene and hydrogen peroxide, respectively.)

The rate constants obtained in this study using both mechanisms provided positive values for both Cr-MCM-48-0.005 and Cr-MCM-48-0.01, as shown in Table 6.2. This could be inferred that both mechanisms were probably acceptable for this work. Interestingly, when considering the three-step mechanism, the values of k_1 and k_3 were the same as those of k_1 and k_2 for the two-step mechanism while the value of k_2 for the three-step mechanism was very high, referring to very fast process. This phenomenon could be interpreted that the three-step mechanism was practically the same as the two-step mechanism.

However, the chromium leaching was easily found in Cr-containing solid catalysts, as described elsewhere [4, 10]. In this case, the chromium ions were

probably leached from the catalyst because the reaction mixture turned purple after adding the catalyst. This situation could be described in terms of the strong complexing and solvolytic properties of oxidants, like H_2O_2 in this case [15]. Moreover, the filtrate after removing the catalyst became yellowish. It might be suggested that chromium ions in the form of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ were oxidized to $[\text{CrO}_4]^{2-}$ in the presence of strong oxidizing agent. Besides the color of reaction mixture, the yellow color of the catalyst was faded out, and this supports the result described earlier.

Catalytic activity of Ce-MCM-48 is summarized in Table 6.3. It was found that the % styrene conversions of all system were quite low, comparing to those of Cr-MCM-48. However, comparing to the system containing no catalyst, % benzaldehyde selectivity significantly increased, especially, either Ce-MCM-48-0.01 or Ce-MCM-48-0.03 catalyst provided the increase of benzaldehyde selectivity from 20.2% to 79.8%. It could be implied that Ce-MCM-48 catalysts preferred benzaldehyde to styrene oxide. These results were in agreement with the results obtained by Wangcheng *et al.* [13]. According to their results, they also informed that Ce cations in the Ce-MCM-41 samples were not active in the oxidation of styrene. In our case, the quantity of catalyst was also studied using Ce-MCM-48-0.03 catalyst (entry 5). As expected, the results showed that % conversion of styrene slightly increased with increasing the amount of catalyst from 0.05g to 0.10g and reached a maximum of 5.1% with 79.0 and 21.0% selectivities of benzaldehyde and styrene oxide, respectively. This could be explained in terms of the increasing of active sites in the system assisted the reaction, as described elsewhere [16, 17]. When the Ce/Si ratio increased up to 0.07, % conversion of styrene was decreased as low as 1.4%, probably resulting from the pore blockage of CeO_2 and hinder active sites. The presence of CeO_2 in Ce-MCM-48-0.01 and Ce-MCM-48-0.07 was investigated by wide angle XRD patterns, as described in the previous work [9].

Furthermore, the nature of the active centers could be resulted in the difference in catalytic manner as well as the product selectivity between Ce and Cr catalyst. These results agreed well with the Gómez *et al.* [4] who found the differences in the oxidation of styrene catalyzed by different metals containing MCM-48.

6.5 Conclusions

Chromium/cerium containing MCM-48 mesoporous materials with edge-truncated octahedral shape were synthesized and used for the styrene oxidation using H_2O_2 as an oxidant. All of the catalysts provided only benzaldehyde and styrene oxide products. The temperature, the amount of styrene and hydrogen peroxide greatly affected to the reaction rate using Cr-MCM-48. Higher metal content provided a faster chemical reaction, supported by the kinetic data. The kinetic studies showed the redox type mechanism and the rate equation from the two-stage mechanism, under a steady state assumption, was proposed to be representative of this reaction. The Ce-MCM-48 catalysts were found to be much less effective than Cr-MCM-48 catalysts.

6.6 Acknowledgements

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6.7 References

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Table 6.1 The catalytic activity results toward the oxidation of styrene using Cr-MCM-48-0.005 and Cr-MCM-48-0.01

Entry	Catalysts	Temperature (°C)	Mole ratio H ₂ O ₂ :styrene	% Conversion	% Selectivity		Initial r (mol.L ⁻¹ h ⁻¹)
					Benzaldehyde	Styrene Oxide	
1	No catalyst	80	1:1	7.5	74.7	25.3	-
2	Cr-MCM-48-0.005	80	0.5:1	28.9	70.4	29.6	2.4
3	Cr-MCM-48-0.005	80	1:1	59.4	74.1	25.9	3.1
4	Cr-MCM-48-0.005	80	2:1	94.3	88.8	11.2	4.1
5	Cr-MCM-48-0.005	80	1:0.5	96.6	87.2	12.8	1.1
6	Cr-MCM-48-0.005	80	1:2	37.2	63.6	36.4	5.1
7	Cr-MCM-48-0.01	80	0.5:1	31.4	80.0	20.0	3.1
8	Cr-MCM-48-0.01	80	1:1	57.0	82.0	18.0	4.1
9	Cr-MCM-48-0.01	80	2:1	91.9	93.9	6.1	6.1
10	Cr-MCM-48-0.01	80	1:0.5	95.1	90.6	9.4	3.1
11	Cr-MCM-48-0.01	80	1:2	34.9	69.0	31.0	6.1
12	Cr-MCM-48-0.005	60	1:1	47.9	77.0	23.1	4 x
13	Cr-MCM-48-0.01	60	1:1	51.5	81.0	19.0	8x
14	Cr-MCM-48-0.005	40	1:1	13.7	97.6	2.4	8x
15	Cr-MCM-48-0.01	40	1:1	21.9	96.3	3.7	10x

Table 6.2 The rate constants calculated from the least squares method of the two-step and the three-step mechanisms using Cr-MCM-48-0.005 and Cr-MCM-48-0.01 as catalysts

Catalysts	Two-step mechanism		Three-step mechanism		
	k_1	k_2	k_1	$k_2 \times 10^4$	k_3
Cr-MCM-48-0.005	0.21	0.40	0.21	7.0	0.40
Cr-MCM-48-0.01	0.34	0.44	0.34	0.8	0.44

Table 6.3 The catalytic activity results toward the oxidation of styrene using Ce-MCM-48 catalysts with the reaction conditions of 80°C, 1:1 of H₂O₂/styrene ratio, and 6h

Entry	Catalyst	Amount of catalyst (g)	% Conversion	% Selectivity	
				Benzaldehyde	Styrene oxide
1	blank	-	3.5	20.2	79.8
2	MCM-48	0.05	3.4	46.2	53.8
3	Ce-MCM-48-0.01	0.05	3.0	79.8	29.4
4	Ce-MCM-48-0.03	0.05	4.9	73.0	27.0
5	Ce-MCM-48-0.03	0.1	5.1	79.0	21.0
6	Ce-MCM-48-0.05	0.05	2.5	77.6	22.4
7	Ce-MCM-48-0.07	0.05	1.4	76.4	23.6

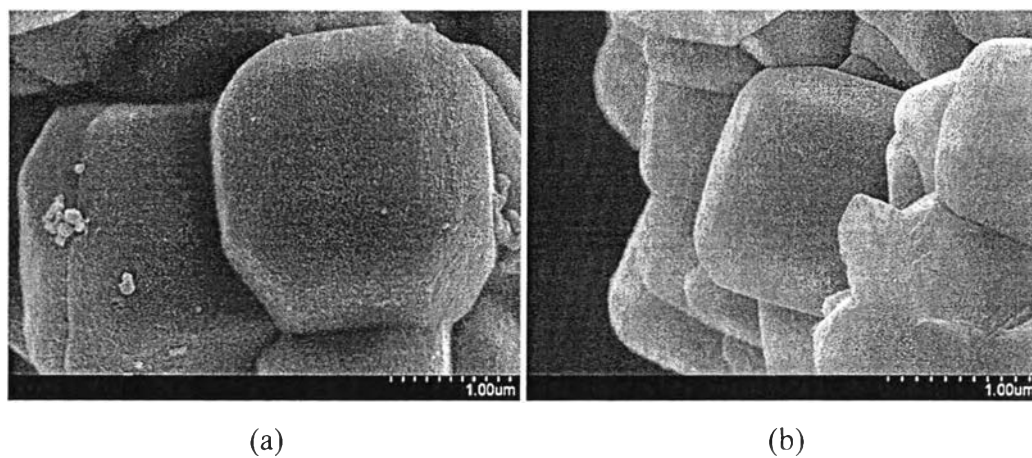
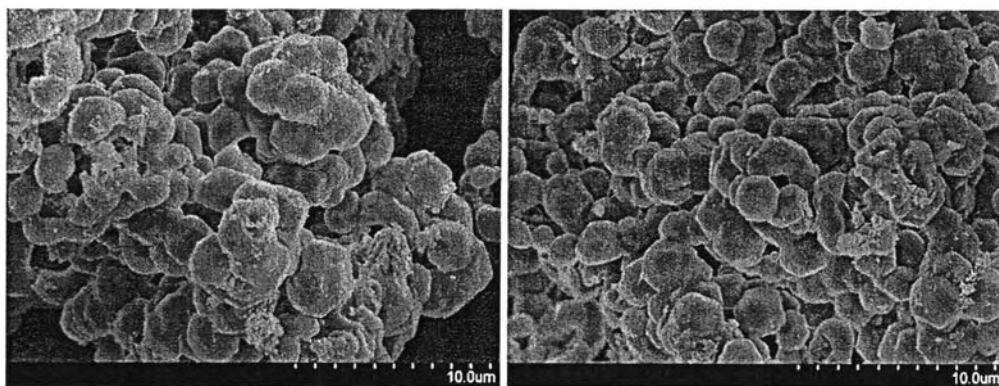
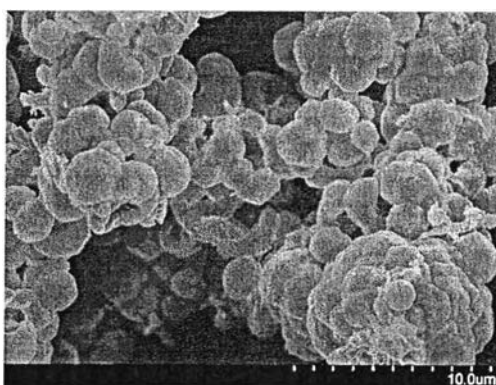


Figure 6.1 SEM images of (a) Cr-MCM-48-0.005 (x30000) and (b) Cr-MCM-48-0.01(x35000).



(a)

(b)



(c)

Figure 6.2 SEM images of (a) Ce-MCM-48-0.01, (b) Ce-MCM-48-0.03 and (c) Ce-MCM-48-0.05 (x5000).

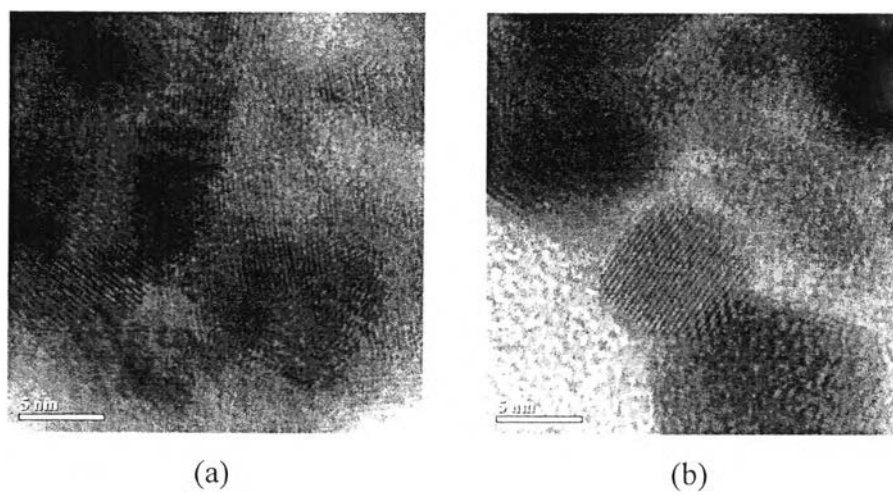


Figure 6.3 TEM images of (a) Cr-MCM-48-0.005 and (b) Cr-MCM-48-0.01 with incident direction along [100].

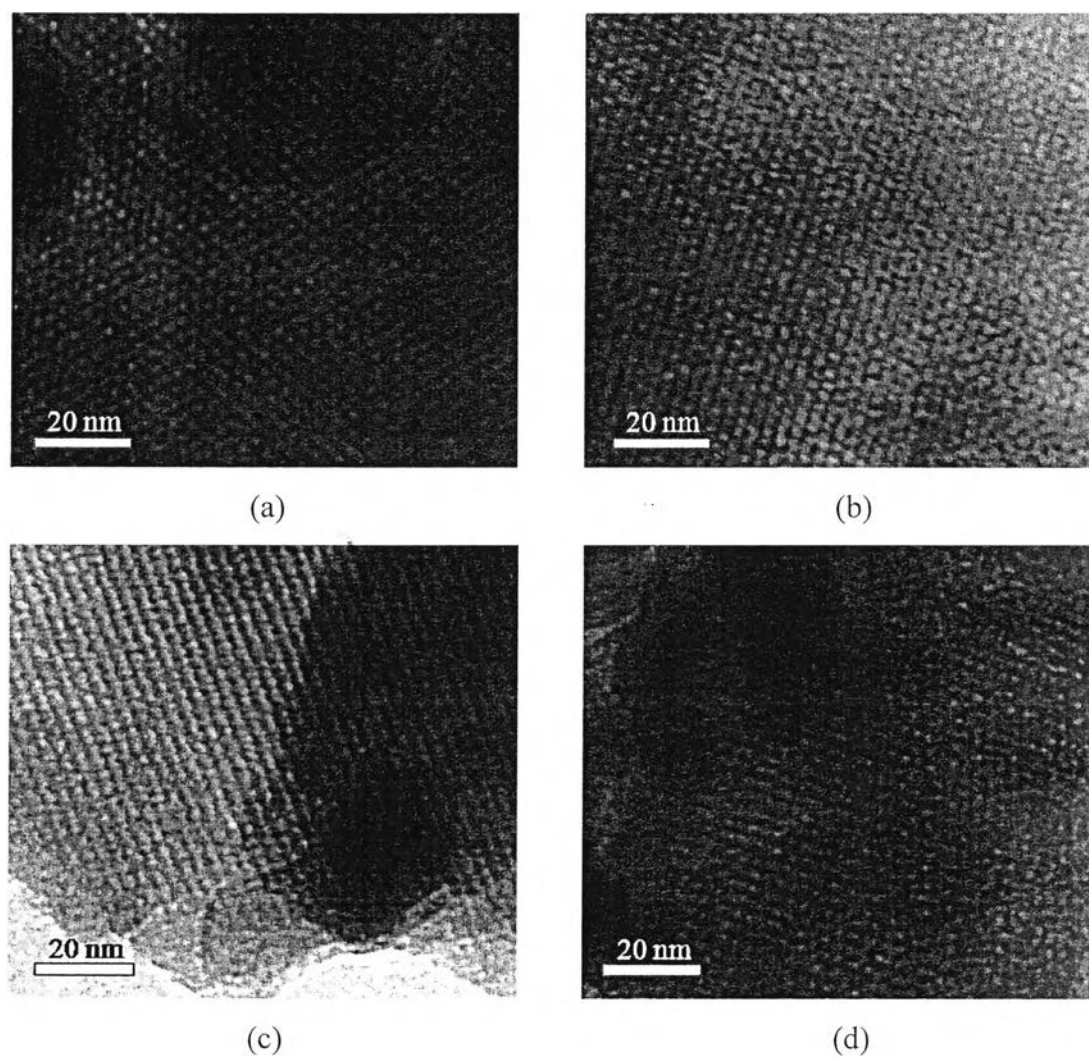


Figure 6.4 TEM images of (a) Ce-MCM-48-0.01 with incident direction along $[531]$, (b) Ce-MCM-48-0.03, (c) Ce-MCM-48-0.05 and (d) Ce-MCM-48-0.07 with incident direction along $[100]$.

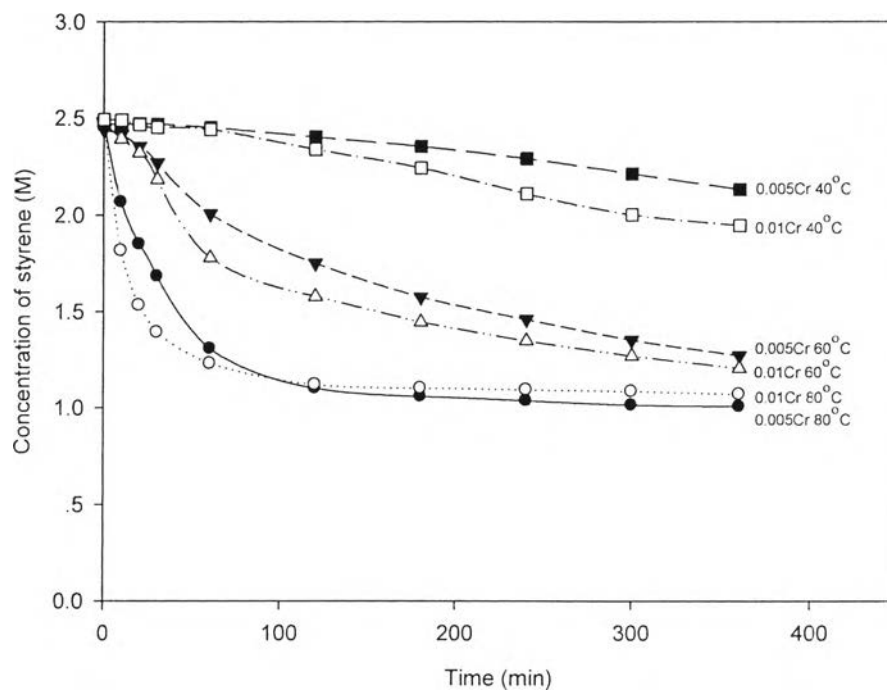


Figure 6.5 The concentration of styrene as a function of time using Cr-MCM-48-0.005 and Cr-MCM-48-0.01 at various reaction temperatures.

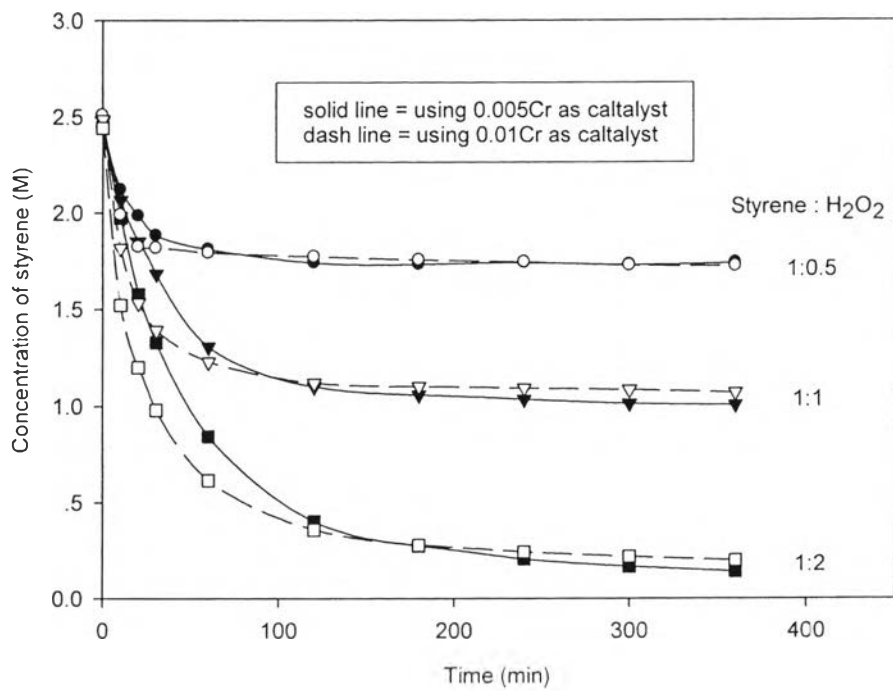


Figure 6.6 The concentration of styrene as a function of time using various H₂O₂/styrene ratios of Cr-MCM-48-0.005 and Cr-MCM-48-0.01.