Cite this article as: Chin J Catal, 2010, 31: 759-764.



**RESEARCH PAPER** 

# Vapor-Phase Alkylation of Phenol with *Tert*-butyl Alcohol Catalyzed by H<sub>3</sub>PO<sub>4</sub>/MCM-41

# Mehran GHIACI\*, Behzad AGHABARARI

Department of Chemistry, Isfahan University of Technology, Isfahan 8415683111, Iran

**Abstract:** The catalytic performance of Al-MCM-41 containing 5-35 wt% H<sub>3</sub>PO<sub>4</sub> was studied for the vapor-phase alkylation of phenol with *tert*-butyl alcohol (TBA) from 383 to 493 K. 4-*Tert*-butyl phenol was produced as the main product with moderate selectivity. The product distribution depends on the reaction temperature, number of acid sites, and the Brönsted to Lewis sites ratios. A lower molar ratio of reactants (TBA/phenol = 2) and a higher space velocity facilitated the production of 4-*tert*-butyl phenol. The influence of various parameters such as temperature, reactant feed molar ratio, feed rate, and time on stream were investigated for conversion yield and product selectivity.

Key words: alkylation; tert-butylation; phenol; tert-butyl alcohol; MCM-41

One of the most important alkyl phenols is 4-*tert*-butylphenol, which has many applications [1-5]. The *t*-butylation of phenol is a typical Friedel-Crafts alkylation and can be catalyzed by acid sites. Numerous studies have been reported on homogeneous and heterogeneous catalysis using several acid catalysts such as Brönsted acids, Lewis acids, activated clay, ionic liquids, and solid acid catalysts in supercritical carbon dioxide [1-4,6,7]. However, homogeneous catalysts are environmentally unfriendly, unselective, and require tedious work-up for the separation of the catalyst. On the other hand, acid catalysts supported on zeolites do not have any of these problems and many have been used for the *t*-butylation of phenol over zeolites such as Y [6,8] and mordenite [7,9] in the gas or liquid phase.

In this reaction, *o*-alkylation is kinetically favored because of the –OH group on the phenol but this product is thermodynamically unfavorable. On the other hand, *ortho*-tertiary butyl phenol (2-TBP) readily isomerizes into the less hindered *p*-isomer (4-TBP) [1,10]. Furthermore, in this reaction the selectivity of the product depends on the nature of the acidic sites present in the catalysts and the reaction temperature [7]. It has been found that *t*-butyl phenyl ether (TBPE) is produced in the presence of weak acidic catalysts as a major product. Under strongly acidic conditions or high temperatures, the reaction produces carbon alkylated products [4,9].

In the last decade, the *t*-butylation of phenol over H-AlMCM-41 [1], Fe-AlMCM-41 [4], sulfated AlMCM-41 with different  $SiO_2/Al_2O_3$  molar ratios [11], MeMCM-41 and MeMCM-48 (Me = Ga, Fe, Al, or B) [12], Zn and Fe containing AlMCM-41 [13] has been studied. In these studies, the researchers have tried to find the best conditions for this reaction to increase the selectivity for 4-TBP and to increase the conversion of phenol [10,14].

In this work we designed a vapor-phase reaction using a moderate solid acid catalyst for the synthesis of *tert*-butylphenol because of the increasing demand for generic procedures in vapor-phase chemistry and the broad range of commercial applications of alkylated phenols. This was done as part of our ongoing research concerned with the development of an environmentally benign chemical process for fine chemical synthesis. In this investigation  $H_3PO_4$  was supported on AIMCM-41 in different proportions. We studied the activity of these catalysts toward the *t*-butylation of phenol in the vapor phase and the results are discussed in detail. We demonstrate that this new catalyst can act as a reusable heterogeneous catalyst for the alkylation of phenol to the corresponding alkylated products.

We have previously reported on the characterization of the

Received date: 26 January 2010.

<sup>\*</sup>Corresponding author. Tel: +98-311-3913254; Fax: +98-311-3912350; E-mail: mghiaci@cc.iut.ac.ir (M. Ghiaci) Foundation item: Research Council of Isfahan University of Technology.

Copyright © 2010, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier BV. All rights reserved. DOI: 10.1016/S1872-2067(09)60085-1

catalysts using <sup>29</sup>Si, <sup>27</sup>Al, <sup>31</sup>P, <sup>23</sup>Na, and <sup>1</sup>H MAS NMR spectroscopy [15]. We have shown that  $H_3PO_4$  loading on AlMCM-41 induces a drastic decrease in the specific surface area without any structural distortion of MCM-41. Therefore, the main reason for choosing these catalysts for the *t*-butylation reaction was that this reaction probably only occurs on the external surface of the catalysts, and the acidity of the catalysts as well as thermodynamic factors greatly affect the conversion and selectivity.

## 1 Experimental

## 1.1 Preparation of the catalysts

The mesoporous molecular sieves Al-MCM-41 and  $H_3PO_4$ /Al-MCM-41 were prepared in accordance with the reported methods [16].

#### 1.2 Catalytic activity

Catalytic tests were performed with the 5 wt% H<sub>3</sub>PO<sub>4</sub>/Al-MCM-41(20) catalysts. The vapor-phase tests were carried out using approximately 0.5 g of catalyst (20-40 mesh) in a feed Pyrex reactor (i.d. 8 mm). The reactor was inserted into an electric oven controlled by a J thermocouple and operated at atmospheric pressure, and the temperature range was 383-493 K. The feed was tert-butyl alcohol (TBA):phenol (2:1 molar ratio), which was introduced by an infusion pump (GENIE, Kent Scientific Corporation) and nitrogen was used as the carrier gas by regulation with a mass-feed meter. The catalyst was previously activated in situ for 1 h at 673 K using a 25 ml/min N<sub>2</sub> feed. In each experiment, the products were collected after 8 h by condensing them in a trap containing salt-ice and cooled to 258 K. Analyses were done off-line using a Shimadzu gas chromatograph (model 14A) equipped with a wide bone OV-17 (60 m) capillary column and an FID detector.

# 2 Results and discussion

#### 2.1 Characterization

The physicochemical characterization of the catalysts was similar to our earlier report [15]. However, other important conclusions that we made from the characterization results are outlined here. The XRD data indicated that the MCM-41 samples exhibit an ordered hexagonal structure characterized by an intense reflection peak at a *d* spacing of 3.8 nm [16]. The intensity of this low angle reflection peak did not change as the  $H_3PO_4$  loading increased. The specific surface area of the samples calculated from the BET method ranges between 1 038 and 668 m<sup>2</sup>/g. Although the  $H_3PO_4$  loading induces a drastic decrease in the surface area, no structural distortions are evident for Al-MCM-41. Consequently, it seems reasonable

that the loading of H<sub>3</sub>PO<sub>4</sub> onto Al-MCM-41 did not change the regular arrangement of the uniform channels of the support [17]. Interestingly, by loading approximately 30 wt% phosphotungstic acid onto Al-MCM-41, the surface area of the support decreases by less than 20% [10], but loading the same support with approximately the same weight percent of H<sub>3</sub>PO<sub>4</sub> results in the surface area decreasing to a larger extent. The crystalline structure of the phosphotungstic acid (Keggin units) and the amorphous structure of the phosphoric acid could explain this difference. The <sup>31</sup>P MAS NMR spectra of the 30 wt% H<sub>3</sub>PO<sub>4</sub>/Al-MCM-41(200) showed two peaks at  $\delta = -10$ and 0, which may correspond to the P atom in pyrophosphoric acid or the terminal and monomeric PO<sub>4</sub><sup>3-</sup> groups, respectively. From an analysis of the Si, Al, and P NMR signals, the formation of Si-O-Al-O-P bridges seems to be favored at the surface of the Al-MCM-41 catalysts. The FT-IR spectra for the 30 wt% H<sub>3</sub>PO<sub>4</sub>/Al-MCM-41(70) containing adsorbed pyridine shows the contribution of pyridine adducts from 1 650-1 450 cm<sup>-1</sup>. The formation of pyridinium ions, as shown by the adsorption at 1 545 and 1 490 cm<sup>-1</sup>, is characteristic of Brönsted acid sites and both Brönsted and Lewis acid sites, respectively. A comparison of the spectra revealed that 30 wt% H<sub>3</sub>PO<sub>4</sub>/ Al-MCM-41(70) possesses a greater amount of acid sites than the other catalysts. The concentration of Brönsted and Lewis acid sites was calculated after evacuation at 473 K using the extinction coefficient of the bands of Brönsted and Lewis acid site adsorbed pyridine [18]. This revealed the presence of high amounts of Brönsted and Lewis acid sites in 30 wt% H<sub>3</sub>PO<sub>4</sub>/Al-MCM-41(70).

## 2.2 Catalytic studies

The vapor phase *t*-butylation of phenol with TBA was carried out over Al-MCM-41 with  $SiO_2/Al_2O_3 = 20$ , 70, and 150, containing 5, 10, and 20 wt% H<sub>3</sub>PO<sub>4</sub>, respectively, from 383 to 493 K. The molar ratio chosen in these experiments for TBA to phenol was 2:1. The major products were 4-*tert*-butyl phenol (4-TBP), 2-*tert*-butyl phenol (2-TBP), and 2,4-di-*tert*-butyl phenol along with less than 5% other products that were not identified. We did not obtain any *tert*-butyl phenyl ether (TBPE) even at high phenol conversion under the best reaction conditions.

The conversion of phenol over Al-MCM-41 with  $SiO_2/Al_2O_3 = 20$ , 70, and 150 was improved with an increase in temperature. The maximum conversion was observed at 463 K and when the temperature reached 493 K the conversion decreased by a few percent (Table 1).

We also observed that TBPE formed at 383 K but it was completely absent at higher temperatures (small amounts of ether formed at 413 K). In the early stages of the reaction, a reversible *O*-alkylation occurs at a high rate because of the low activation energy on almost all the acid sites (independent of acid strength). The decrease in TBPE selectivity with increas-

| Cotalyst  | Temperature (K) | Phenol conversion (%) | Product selectivity (%) |       |       |          |        |  |
|---|-----------------|-----------------------|-------------------------|-------|-------|----------|--------|--|
| Catalyst  |                 |                       | TBPE                    | 2-TBP | 4-TBP | 2,4-DTBP | Others |  |
| 5 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(20)   | 383             | 35.7                  | 30.1                    | 25.5  | 22.7  | 21.2     | 0.5    |  |
|   | 413             | 40.2                  | 1.9                     | 32.6  | 34.7  | 30.1     | 0.7    |  |
|   | 443             | 44.9                  | _                       | 19.3  | 43.9  | 35.8     | 1.0    |  |
|   | 463             | 47.7                  | _                       | 15.0  | 62.6  | 19.1     | 3.3    |  |
|   | 493             | 36.8                  | _                       | 11.2  | 66.6  | 17.9     | 4.3    |  |
| 10 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(70)  | 383             | 47.5                  | 26.3                    | 25.7  | 24.2  | 23.6     | 0.2    |  |
|   | 413             | 49.4                  | 1.0                     | 34.9  | 37.6  | 26.2     | 0.3    |  |
|   | 443             | 54.3                  | _                       | 26.9  | 50.40 | 21.6     | 1.1    |  |
|   | 463             | 57.1                  | —                       | 17.8  | 68.2  | 10.1     | 3.9    |  |
|   | 493             | 48.8                  | _                       | 13.1  | 69.5  | 12.9     | 4.5    |  |
| 20 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(150) | 383             | 33.6                  | 29.5                    | 23.8  | 22.2  | 24.2     | 0.3    |  |
|   | 413             | 37.4                  | 3.3                     | 30.7  | 36.2  | 29.2     | 0.6    |  |
|   | 443             | 48.6                  | _                       | 31.6  | 39.4  | 27.5     | 1.5    |  |
|   | 463             | 54.1                  | —                       | 15.6  | 61.0  | 21.6     | 1.8    |  |
|   | 493             | 41.9                  | _                       | 18.6  | 56.8  | 20.2     | 4.4    |  |

Table 1 Effect of temperature on the *t*-butylation of phenol over 5 wt%  $H_3PO_4/Al-MCM-41(20)$ , 10 wt%  $H_3PO_4/Al-MCM-41(70)$ , and 20 wt%  $H_3PO_4/Al-MCM-41(150)$ 

Reaction conditions: TBA/phenol molar ratio = 2, WHSV =  $1.41 h^{-1}$ , time on stream = 2.5 h, catalyst = 0.5 g.

ing temperature may be due to rearrangement to a *C*-alkylated product. It has been shown that such a rearrangement occurs on heating or by contact with an acid catalyst [8,19].

The gradual increase in conversion of phenol from 383 to 463 K may be due to a predominant *C*-alkylation over *O*-alkylation at higher temperatures and also the conversion of *O*-alkylated to *C*-alkylated products. The major product was found to be 4-TBP. A comparison of the product distribution at 383–463 K showed a low percentage of undesired products for all the catalysts. This is important because the undesired products may especially consume TBA without producing the desired *C*-alkylated phenols, which leads to a low phenol conversion. The decrease in conversion at higher temperature (493 K) may also be due to the partial blocking of pores and active sites by coke or polybutene formation [10].

The selectivity for 4-TBP was higher than for both 2-TBP and 2,4-DTBP at temperatures higher than 383 K. The *ortho/para* ratio of the *C*-alkylated products reduces with an increase in temperature. The increase in selectivity for 4-TBP is proportional to the decrease in selectivity for 2-TBP and 2,4-DTBP, which is consistent with an increase in the rate of dealkylation and it reaches an approximate equilibrium condition. Consequently, the rearrangement reaction during the alkylation process will change the distribution of the alkyl phenols. The continuous migration from *o*-alkylphenol to *p*-alkylphenol is a thermodynamically driven process because the latter is energetically more stable [19].

A few reports [6,10] demonstrate that the observed increase in *para* selectivity is accompanied by a decrease in phenol conversion. In this respect, we think that the acidic strength of the catalyst plays an important role. The presence of strong Brönsted acid sites promotes side reactions of TBA such as oligomerization and aromatization [1,20]. For this work, we assumed that  $H_3PO_4$  replaced most of the strong Brönsted acid sites by moderate acid sites [15] and this decreases TBA oligomerization [1,10].

#### 2.2.1 Effect of H<sub>3</sub>PO<sub>4</sub>

Different quantities of  $H_3PO_4$  were loaded on Al-MCM-41(70) using the incipient wetness technique. It has been found that the selectivity for 2-TBP is highly dependent on the amount of  $H_3PO_4$  loaded on Al-MCM-41(70). With an increase in  $H_3PO_4$  loading from 5 to 30 wt%, the conversion of phenol increased from 52% to 79%, respectively. The 35 wt%  $H_3PO_4/Al-MCM-41(70)$  catalyst gave less conversion compared with the 30 wt%  $H_3PO_4/Al-MCM-41(70)$  catalyst and this is probably due to the masking of active sites. An optimum selectivity for 4-TBP (~79%) at a conversion of about 79% was obtained when 30 wt%  $H_3PO_4$  was impregnated onto Al-MCM-41(70) (Table 2).

## 2.2.2 Effect of the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio

To investigate the effect of Si/Al on the catalytic activity for the alkylation of phenol with TBA in the vapor phase, we tested different Al-MCM-41 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio = 20–200) with 30 wt% H<sub>3</sub>PO<sub>4</sub> at 463 K. As noted in the experimental section, the catalysts were activated in situ for 1 h at 673 K under a 25 ml/min feed of N<sub>2</sub> before the catalytic run. Therefore, no water was present on the fresh catalyst surface. The experiments were carried out at a molar ratio of TBA/phenol = 2.

| C-t-last  | Phenol conversion (%) | Product selectivity (%) |       |       |          |        |  |
|---|-----------------------|-------------------------|-------|-------|----------|--------|--|
| Catalyst  |                       | TBPE                    | 2-TBP | 4-TBP | 2,4-DTBP | Others |  |
| Al-MCM-41(70)   | 45.3                  | —                       | 27.2  | 61.1  | 8.5      | 3.2    |  |
| 5 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(70)   | 52.2                  | —                       | 20.6  | 67.8  | 8.7      | 2.9    |  |
| 10 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(70)  | 57.1                  | —                       | 17.8  | 68.2  | 10.1     | 3.9    |  |
| 15 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(70)  | 65.5                  | —                       | 14.6  | 70.0  | 10.3     | 5.1    |  |
| 20 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(70)  | 62.5                  | —                       | 12.2  | 71.2  | 11.2     | 5.4    |  |
| 25 wt% H <sub>3</sub> PO <sub>4</sub> / Al-MCM-41(70) | 70.7                  | —                       | 8.1   | 75.2  | 12.3     | 4.4    |  |
| 30 wt% H <sub>3</sub> PO <sub>4</sub> / Al-MCM-41(70) | 78.6                  | —                       | 5.7   | 79.1  | 12.5     | 2.7    |  |
| 35 wt% H <sub>3</sub> PO <sub>4</sub> / Al-MCM-41(70) | 75.4                  | —                       | 6.1   | 72.2  | 15.8     | 5.9    |  |

 Table 2
 Effect of H<sub>3</sub>PO<sub>4</sub> weight percent on the *t*-butylation of phenol over Al-MCM-41(70)

Reaction conditions: catalyst = 0.5 g, temperature = 463 K, TBA/phenol molar ratio = 2, WHSV = 1.41 h<sup>-1</sup>, time on stream = 2.5 h.

As shown in Fig. 1, phenol conversion over 30 wt%  $H_3PO_4/Al-MCM-41(70)$  was higher than that for the other catalysts. The catalysts with a high hydrophilic character (low Si/Al framework ratio) are the most active catalysts because of their improved adsorption properties for polar molecules [7]. Therefore, we chose Al-MCM-41(70) as the best catalyst for further studies.

## 2.2.3 Effect of molar ratio

Figure 2 demonstrates the effect of TBA to phenol molar ratio on the *t*-butylation reaction of phenol over the 30 wt%  $H_3PO_4/Al-MCM-41(70)$  catalyst. It can be seen from the figure that phenol conversion increases with an increase in the TBA to phenol molar ratio. This data is in agreement with the literature [10] because the increase in conversion might be due to increased chemisorption of the TBA over the catalyst surface and the greater availability of *t*-butyl cations near the chemisorbed phenol. However, the increase in TBA content leads to a decrease in monoalkylated product selectivity because of a possible secondary alkylation reaction resulting in the formation of



**Fig. 1.** Effect of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio on the *t*-butylation of phenol over 30 wt% H<sub>3</sub>PO<sub>4</sub>/Al-MCM-41(70). Reaction conditions: catalyst = 0.5 g, temperature = 463 K, TBA/phenol molar ratio = 2, WHSV = 1.41 h<sup>-1</sup>, time on stream = 2.5 h.

2,4-DTBP. From Fig. 2, the selectivity for 4-TBP decreases with an increase in the TBA content of the feed. The extent of decrease in 4-TBP selectivity was drastic when the molar ratio was changed from 2:1 to 3:1. At higher TBA to phenol molar ratios the selectivity for 4-TBP decreased and the undesired product selectivity increased. From the results of phenol conversion and 4-TBP selectivity (desired product), a molar ratio of 2:1 was chosen as the optimum for further studies.

## 2.2.4 Effect of WHSV

The conversion of phenol increased with an increase in WHSV from 0.564 to  $1.41 \text{ h}^{-1}$  and beyond this  $(1.692 \text{ h}^{-1})$ , a decrease was observed (Fig. 3). This increase in phenol conversion suggests the clustering of phenol at a lower WHSV, which suppresses alkylation whereas at higher WHSV the dispersal of phenol facilitates high conversion. At higher than  $1.41 \text{ h}^{-1}$ , the conversion decreases because of the rapid diffusion of phenol from the surface of the catalyst, which may be responsible for the reduced reaction. Therefore, a negative WHSV effect was clearly observed at higher than  $1.41 \text{ h}^{-1}$ . The selectivity for 4-TBP and 2-TBP remains nearly the same with



**Fig. 2.** Effect of TBA/phenol molar ratio on the *t*-butylation of phenol over 30 wt%  $H_3PO_4$ /Al-MCM-41(70). Reaction conditions: catalyst = 0.5 g, temperature = 463 K, WHSV = 1.41 h<sup>-1</sup>, time on stream = 2.5 h.



**Fig. 3.** Effect of WHSV on the *t*-butylation of phenol over 30 wt%  $H_3PO_4/AI$ -MCM-41(70). Reaction conditions: catalyst = 0.5 g, temperature = 463 K, TBA/phenol molar ratio = 2, time on stream = 2.5 h.

an increase in WHSV. This observation indicates that the catalyst may be useful in maintaining the selectivity of the products over a WHSV range.

## 2.2.5 Effect of time on stream

Catalyst deactivation by coke deposition or by the formation of polybutenes was not of consequence in this study. Therefore, the selectivity for 4-TBP was almost constant (Fig. 4) and the slight decrease in conversion or selectivity did not appear to be important. The selectivity for 2,4-DTBP showed a slight increase with an increase in time on stream as a result of the slight decrease in selectivity for 4-TBP. 2-TBP may not be a significant contributing factor to the selectivity for 2,4-DTBP as it did not show a decrease in selectivity with time on stream. From these observations, we conclude that the adsorption of 4-TBP or 2-TBP is largely prevented compared to phenol and hence both the 2-TBA and 4-TBP that remain in the vapor phase react with the *tert*-butyl cation [21].



**Fig. 4.** Effect of time on stream on the *t*-butylation of phenol over 30 wt%  $H_3PO_4$ /Al-MCM-41(70). Reaction conditions: catalyst = 0.5 g, temperature = 463 K, TBA/phenol molar ratio = 2.

The data in Table 3 shows a comparison of the results obtained over 30 wt%  $H_3PO_4/Al-MCM-41(70)$  and the other catalysts used in this reaction. In fact, the catalyst used in this study might be one of the best catalysts with regards to phenol conversion and selectivity for 4-TBP (yield of 4-TBP) and with regards to the simplicity of the synthetic method.

# **3** Conclusions

In this work, we demonstrate the applicability of a new catalyst containing moderate and weak Brönsted acid sites for the alkylation of phenol. A series of  $H_3PO_4$  loaded Al-MCM-41 catalysts were synthesized and characterized by various NMR methods. The vapor phase alkylation of phenol over these catalysts showed that the catalyst containing 30 wt%  $H_3PO_4$  supported on Al-MCM-41 had the highest activity. The absence of multialkylation and the catalyst's high activity over 15 h on stream as well as negligible catalyst.

Table 3 Comparison between 30 wt% H<sub>3</sub>PO<sub>4</sub>/Al-MCM-41(70) and the other catalysts for phenol conversion and 4-TBP selectivity

| Catalyst   | Phenol conversion (%) | Product selectivity (%) |       |       |          | Viald of 4 TDD | D-f       |
|--|-----------------------|-------------------------|-------|-------|----------|----------------|-----------|
|  |                       | TBPE                    | 2-TBP | 4-TBP | 2,4-DTBP | Tield of 4-TBP | KeI.      |
| 20 wt% PW/Al-MCM-41                                  | 88.7                  | _                       | 6.0   | 83.7  | 10.3     | 74.24          | [10]      |
| 30 wt% H <sub>3</sub> PO <sub>4</sub> /Al-MCM-41(70) | 78.6                  | _                       | 5.7   | 79.1  | 12.5     | 62.17          | this work |
| 30%PW/SBA-15   | 70.1                  |                         | 6.6   | 79.2  | 14.2     | 55.52          | [21]      |
| Fe,Al-MCM-41   | 70.1                  |                         | 10.4  | 75.2  | 14.4     | 52.71          | [4]       |
| AlSBA-15 (45) (Ex)                                   | 62.9                  |                         | 7.7   | 80.9  | 11.3     | 50.89          | [22]      |
| Sulfated zirconia                                    | 57.8                  | _                       | 6.8   | 86.5  | 6.7      | 50.00          | [20]      |
| Zeolite, HY  | 97.1                  | _                       | 2.0   | 50.9  | 47       | 49.42          | [8]       |
| H-GaMCM-48   | 63.6                  |                         | 10.1  | 76.5  | 10.5     | 48.65          | [12]      |
| НҮ   | 69.4                  | 0.5                     | 6.4   | 68.8  | 9.8      | 47.74          | [6]       |
| 20 wt% PW/AlPO                                       | 57.0                  | 16.0                    | 7.9   | 76.0  | _        | 43.32          | [18]      |
| Al-MCM-41(56)  | 35.9                  | _                       | 8.1   | 83.4  | 3.9      | 29.94          | [1]       |
| 15% MPA/ZrO <sub>2</sub>                             | 80.6                  |                         | 11.5  | 25.7  | 55.2     | 20.71          | [19]      |

## Acknowledgments

We thank the Research Council of the Isfahan University of Technology and the Center of Excellence in the Chemistry Department of Isfahan University of Technology for supporting of this work.

# References

- Sakthivel A, Badamali S K, Selvam P. Microporous Mesoporous Mater, 2000, 39: 457
- 2 Krishnan A V, Ojha K, Pradhan N C. Org Process Res Dev, 2002, 6: 132
- 3 Yadav G D, Doshi N S. Appl Catal A, 2002, 236: 129
- 4 Vinu A, Nandhini K U, Murugesan V, Böhlmann W, Umamaheswari V, Pöppl A, Hartmann M. *Appl Catal A*, 2004, **265**: 1
- 5 Kumar G S, Saravanamurugan S, Hartmann M, Palanichamy M, Murugesan V. J Mol Catal A, 2007, 272: 38
- 6 Anand R, Maheswari R, Gore K U, Tope B B. J Mol Catal A, 2003, 193: 251
- 7 Dumitriu E, Hulea V. J Catal, 2003, 218: 249
- 8 Zhang K, Zhang H, Xu G, Xiang S, Xu D, Liu S, Li H. Appl Catal A, 2001, 207: 183
- 9 Zhang K, Xiung S H, Zhang H B, Liu S Y, Li H X. React Kinet

Catal Lett, 2002, 77: 13

- 10 Nandhini K U, Mabel J H, Arabindoo B, Palanichamy M, Murugesan V. *Microporous Mesoporous Mater*, 2006, 96: 21
- 11 Ng E-P, Nur H, Wong K-L, Muhid M N M, Hamdan H. Appl Catal A, 2007, 323: 58
- 12 Selvam P, Dapurkar S E. Catal Today, 2004, 96: 135
- 13 Savidha R, Pandurangan A, Palanichamy M, Murugesan V. J Mol Catal A, 2004, 211: 165
- 14 Nandhini K U, Arabindoo B, Palanichamy M, Murugesan V. J Mol Catal A, 2004, 223: 201
- 15 Ghiaci M, Aghaei H, Oroojeni M, Aghabarari B, Rives V, Vicente M A, Sobrados I, Sanz J. Catal Commun, 2009, 10: 1486
- 16 Ghiaci M, Abbaspur A, Kia R, Belver C, Trujillano R, Rives V, Vicente M A. Catal Commun, 2007, 8: 49
- 17 Melo R A A, Giotto M V, Rocha J, Urquieta-Gonzalez E A. Mater Res, 1999, 2: 173
- 18 Nandhini K U, Arabindoo B, Palanichamy M, Murugesan V. J Mol Catal A, 2006, 243: 183
- 19 Devassy B M, Shanbhag G V, Halligudi S B. J Mol Catal A, 2006, 247: 162
- 20 Sakthivel A, Saritha N, Selvam P. Catal Lett, 2001, 72: 225
- 21 Kumar G S, Vishnuvarthan M, Palanichamy M, Murugesan V. J Mol Catal A, 2006, 260: 49
- 22 Chandrasekar G, Hartmann M, Palanichamy M, Murugesan V. Catal Commun, 2007, 8: 457