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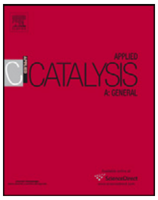

# A simple and efficient zeolite catalyst for toluene oxidation in aqueous media

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## ABSTRACT

In this work, it was found that alkali-treated zeolites could efficiently catalyze oxidation of toluene with $H_2O_2$ in aqueous media. No heavy metals or their oxides were employed in the synthesis of catalyst and no additives were used in this catalytic system. Through optimizing the experimental conditions, alkali-treated HZSM-5 exhibited good catalytic activity for toluene oxidation in only 5 h at a low temperature (below 100 °C): 32.0% conversion of toluene with selective formation of 25.0% benzaldehyde, 20.8% benzyl alcohol and 27.5% benzoic acid. Moreover, the results of reusability studies indicated that alkali-treated HZSM-5 was a durable and green catalyst for toluene oxidation in aqueous media. The changes in acidities and textural features of the zeolites induced by alkali-treatment were characterized by ammonia temperature programmed desorption ($NH_3$-TPD) and X-ray powder diffraction (XRD), respectively. The results indicated the reactivity for toluene oxidation could be related to the amount of species $\equiv Al^{\bullet}$ and $\equiv AlOH$ in this system. A probable redox mechanism for toluene oxidation catalyzed by alkali-treated zeolites in aqueous media was proposed in this work.

## 1. Introduction

Using water as the desirable solvent in organic reactions has received a great deal of attentions and shows significant environmental advantages [1–3]. In organic synthesis, it has been found out that a variety of reactions [4–8], including Claisen rearrangement, Michael addition, Mannich and Diels–Alder reaction, could be accelerated in aqueous media. However, some reactions proceed slowly when pure water is employed as the sole medium due to the hydrophobicity of organic molecules. In order to facilitate these reactions, modification of the hydrophobic reagents and employment of organic cosolvents, phase-transfer catalysts, or surfactants in the reaction processes had been widely investigated [9–13]. In recent years, the research focusing on the development of efficient heterogeneous catalysts for the organic reactions in aqueous media has aroused great interests. Various polymer-supported catalysts [14–16] with rare earth metals as active sites have been successfully produced and have exhibited highly catalytic activity in water for C—C bond formation reactions. Meanwhile, some inorganic materials [17–19] (e.g. amorphous $SiO_2$) that possess good hydrothermal and mechanical stabilities are also considered as excellent supports to develop heterogeneous catalyst. Kim et al. [19] prepared a Lewis acid solid via immobilization of Lanthanum sulfonate on SBA-15 and used it to catalyze the Diels–Alder and allylation reactions of carbonyl compounds with aqueous media. Besides its advantages in C–C bond formation reactions, water is also a promising medium for the selective oxidation of carbonyl compounds [20].

The catalytic oxidation of toluene has been investigated with great efforts during the past decades. The primary products in selective oxidation of toluene are important organic intermediates, including benzaldehyde, benzyl alcohol and benzyl acid. In deep oxidation of toluene, the formation of carbonaceous deposits (coke) [21] that are mainly composed of aromatic hydrocarbons and oxygenated aromatic compounds, leads to the deactivation of the catalysts in the fix-bed system. The formation and then the removal of coke resulted in a great increase of costs for the industrial production. What's more, in the traditional process of using toluene oxidation to produce benzaldehyde and benzyl alcohol, the employment of inorganic oxidants (e.g. $KMnO_4$ or $CrO_3$) inevitably generates toxic waste and hazardous byproducts, which are harmful to the environment [22]. By now, great efforts [23–28] have been made to develop new efficient catalytic systems in liquid-phase using non-toxic oxidant ($O_2$ or air) from the environmental viewpoint. In these catalytic systems, heavy metals or their oxides were widely used as active component in the synthesis of catalysts and additives were also employed to improve the reactivity of toluene oxidation in some cases. Recently, a major breakthrough in this field had been made. Single metal or bimetallic catalyst was hired in $O_2$ or air oxidation of toluene with or without solvent, especially Hutchings et al. [29] reported that they could selectively oxidize toluene to give benzyl benzoate by using Au–Pd alloy nanoparticles with a very high selectivity.

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Here we proposed an effective heterogeneous catalytic system employing aqueous media for the oxidation of toluene. In this reaction, a series of zeolites and alkali-treated zeolites were used as heterogeneous catalysts in water with $H_2O_2$ as the oxidant. According to the report on the TS-1/$H_2O_2$ system [30], the employment of water as the solvent led to significant enhancement in the reaction rates in the hydroxylation of toluene, while the products (benzaldehyde, benzyl alcohol and benzyl acid) of the toluene oxidation could not be detected. However, the alkali-treated HZSM-5 exhibited good catalytic activity for toluene oxidation in aqueous media in only 5 h at a low temperature (below 100 °C). The investigation on the oxidation of benzaldehyde and benzyl alcohol could be helpful to comprehend the selectivities for benzaldehyde, benzyl alcohol, benzoic acid and phenols in this catalytic system. To the best of our knowledge, alkali-treated zeolites were firstly used as heterogeneous catalysts for oxidation of toluene in aqueous media with $H_2O_2$. In the absence of heavy metals and additives, this catalytic system is simple, efficient and environment-friendly.

## 2. Experimental

### 2.1. Catalyst preparation

The zeolites (HZSM-5, NaZSM-5 and HBeta, $SiO_2/Al_2O_3 = 25$, obtained from Catalyst Factory of NanKai University) were calcined in air at 550 °C for 6 h before the alkali-treatment. After the precalcination, 4.0 g of zeolite was added into the NaOH solution. The mixture was stirred at 80 °C for 2 h. The resulting zeolite was recovered by filtration and washed with distilled water until a neutral filtrate was received. The obtained white powder was dried at 110 °C for 12 h. The concentration of NaOH solution varied from 0 to 0.40 mol/L. The alkali-treated HZSM-5 and NaZSM-5 were denoted as HZSM-5-*x* and NaZSM-5-*x*, respectively, where *x* represented the concentration of NaOH solution.

The structure of the zeolites was characterized by X-ray powder diffraction (XRD). The XRD patterns of samples were recorded on a Rigaku D/max-2500 diffractometer through a $2\theta$ range from 5° to 80° using Cu$K\alpha$ radiation at 40 kV and 100 mA. Temperature-programmed desorption of ammonia ($NH_3$-TPD) was performed on a chemisorption analyzer (Quanta-chrome ChemBet 300). 0.1 g of sample was preheated at 450 °C under flowing He for 1 h to remove physisorbed species, then cooled to 100 °C. The sample was saturated with 5% $NH_3$/Ar and then purged by He gas to remove excessive physisorbed ammonia. Desorption of ammonia was performed in the temperature range of 100–600 °C at a rate of 10 °C/min. The $^{27}$Al MAS NMR experiments were carried out by a Varian Infinityplus 400 MHz NMR spectrometer.

### 2.2. Catalytic reactions

The oxidation of toluene was carried out in a three-necked flask equipped with a refluxing condenser. In such a typical experiment, toluene (20.0 mmol) and catalyst were added to distilled water (24.0 ml) under vigorous stirring. The mixture was heated to refluxing followed by the dropping of a certain amount of $H_2O_2$ into the mixture. The mixture was refluxed for a certain time under atmosphere, and then cooled to room temperature. The recovery of the product was extracted by 20 ml of ethyl acetate for three times. Conversions and selectivities were determined by gas chromatography with a SGE AC20 capillary column (polyethylene glycol, 30 m × 0.32 mm × 0.50 μm), and the product was identified by $^1$H NMR spectroscopy.

## 3. Results and discussion

The powder XRD patterns of the samples are shown in Fig. 1. It was clear that all the samples exhibited typical MFI structure. Though the NaOH solution would dissolve Si atoms from the zeolite framework, the specific MFI structure had been preserved after the alkali-treatment. Among the alkali-treated HZSM-5 samples, HZSM-5-0.05, HZSM-5-0.10 and HZSM-5-0.20 exhibited almost the same powder XRD patterns as that of the parent zeolite HZSM-5 (Fig. 1A). In the patterns of these samples, no obvious decrease in the relative crystallinity could be observed. On the contrary, the employment of NaOH solution with higher concentration (0.3 and 0.4 mol/L) resulted in lower relative crystallinity of the zeolites, which is attributed to the extraction of Si and Al atoms from framework [31]. The relationship between specific MFI structure of the microporous zeolite and concentration of alkali-treated solution would also be displayed when NaZSM-5 zeolite was employed as the parent sample. As shown in Fig. 1B, the relative crystallinity of the samples decreased after NaZSM-5 zeolite was treated under severe conditions. For comparison, HBeta zeolite was also treated with alkaline solution. Even though mild conditions of alkali-treatment were employed, the typical structure of HBeta zeolite was destructed evidently (Fig. 1C). It suggested that HZSM-5 and NaZSM-5 showed higher stability toward alkali-treatment than HBeta. In addition, it could be affirmed that the alkali-treatment under severe conditions could cause the destruction of zeolite structure.

The $NH_3$-TPD method was used to characterize the amount and acid strength of acid sites in zeolites and the profiles are shown in Fig. 2. The profiles of all the HZSM-5-*x* samples (Fig. 2A) exhibited broad peaks in the temperature region from 100 °C to 500 °C. For the profile of HZSM-5, the peak corresponding to low temperature, which centered at around 200 °C, could be attributed to the $NH_3$ chemisorbed on the weak acid sites. These acid sites were related to the interaction between ammonia molecules and surface oxide or hydroxyl groups by non-specific hydrogen bonding [32]. In the high temperature region, the peak which centered at 450 °C could be ascribed to the strong acid sites. For the profile of HZSM-5-0.20, the strong acid sites disappeared with the reinforcement of medium acid sites. A comparison between HZSM-5-0.40 and HZSM-5-0.20 indicated a decrease in medium acidity for the reason that the framework Al atoms was seriously dissolved in the alkaline solution under severe condition. Two distinct $NH_3$ desorption peaks were observed for the profiles of NaZSM-5 and alkali-treated NaZSM-5 (Fig. 2B), indicating that two types of acid sites with different acid strengths existed on the zeolite. For the sample alkali-treated under severe conditions, the amount of medium acid sites decreased obviously. The results of $NH_3$-TPD suggested the medium and strong acid sites are more sensitive to alkaline solution than the weak acid sites [31].

Series of zeolites, amorphous $SiO_2$ and $Al_2O_3$ were employed as catalysts for the oxidation of toluene. The results are listed in Table 1. All of the parent zeolites showed certain oxidation activity in contrast to amorphous $SiO_2$ and $Al_2O_3$. The oxidation by NaZSM-5 gave 16.2% conversion of toluene which was higher than those of HZSM-5 and HBeta zeolite. The alkali-treated HBeta zeolite presented no catalytic activity for the oxidation of toluene. So did the amorphous $SiO_2$ and $Al_2O_3$. As it had been described by powder XRD, the specific structure of HBeta zeolite was seriously destroyed during the alkali-treatment. Therefore, it could be deduced that the catalytic active sites should locate in the framework of zeolites. According to the results of $NH_3$-TPD, medium acid sites were generated in zeolites via the alkali-treatment that caused the variation of acidity for HZSM-5 and NaZSM-5. Hence, the alkali-treated zeolites were tested in the oxidation of toluene with $H_2O_2$ (Table 1). Among all these samples, HZSM-5-0.20 performed the highest

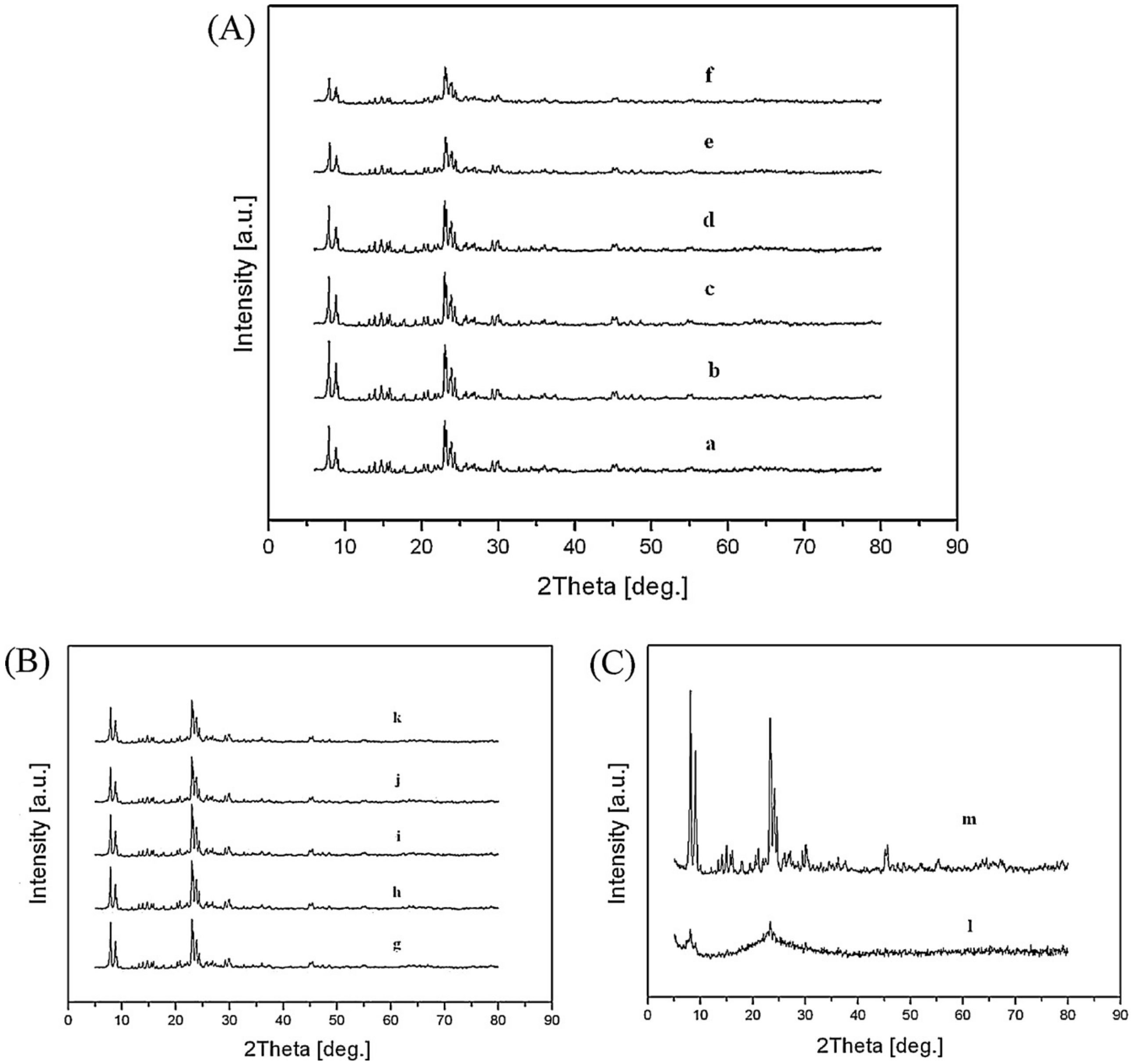

**Fig. 1.** (A) Powder XRD patterns of HZSM-5 and alkali-treated HZSM-5: (a) HZSM-5, (b) HZSM-5-0.05, (c) HZSM-5-0.10, (d) HZSM-5-0.20, (e) HZSM-5-0.30 and (f) HZSM-5-0.40; (B) Powder XRD patterns of NaZSM-5 and alkali-treated NaZSM-5: (g) NaZSM-5, (h) NaZSM-5-0.05, (i) NaZSM-5-0.10, (j) NaZSM-5-0.20 and (k) NaZSM-5-0.30; (C) Powder XRD patterns of (l) HBeta and (m) HBeta-0.20.

**Table 1**
The performance of amorphous $SiO_2$, $Al_2O_3$, parent zeolites and alkali-treated zeolites for the oxidation of toluene.[a]

| Catalyst | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|
| | | Benzaldehyde | Benzyl alcohol | Benzoic acid | Phenols |
| HZSM-5 | 5.9 | 52.4 | 22.9 | 14.6 | 3.3 |
| HZSM-5-0.05 | 20.2 | 40.8 | 26.0 | 14.8 | 14.5 |
| HZSM-5-0.10 | 23.2 | 26.9 | 27.3 | 22.2 | 18.6 |
| HZSM-5-0.20 | 32.0 | 25.0 | 20.8 | 27.5 | 22.3 |
| HZSM-5-0.30 | 18.1 | 40.2 | 22.1 | 17.0 | 17.9 |
| HZSM-5-0.40 | 9.5 | 49.2 | 21.4 | 8.8 | 14.3 |
| NaZSM-5 | 16.2 | 38.1 | 22.8 | 9.0 | 26.7 |
| NaZSM-5-0.05 | 20.5 | 23.9 | 17.8 | 12.6 | 41.2 |
| NaZSM-5-0.10 | 24.9 | 21.7 | 18.7 | 17.7 | 37.7 |
| NaZSM-5-0.20 | 17.0 | 31.2 | 19.6 | 13.5 | 31.2 |
| NaZSM-5-0.30 | 10.2 | 39.1 | 20.1 | 8.9 | 27.6 |
| HBeta | 2.1 | 37.6 | 19.7 | 2.4 | 6.0 |
| HBeta-0.20 | <1 | – | – | – | – |
| $Al_2O_3$ or $SiO_2$ | <1 | – | – | – | – |
| Blank | <1 | – | – | – | – |

[a] Reaction conditions: toluene (20.0 mmol), catalyst (0.125 g), $H_2O$ (24.0 ml), $H_2O_2$ (8.0 ml), refluxing for 5 h.

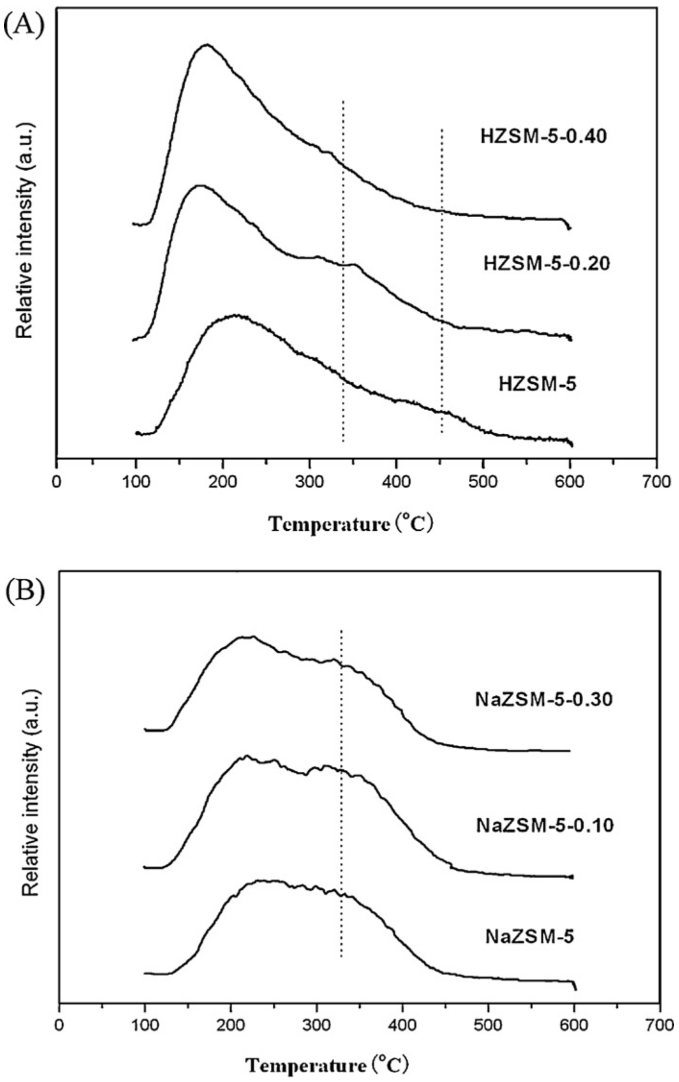

**Fig. 2.** $NH_3$-TPD profiles of (A) HZSM-5, HZSM-5-0.20 and HZSM-5-0.40; (B) NaZSM-5, NaZSM-5-0.10 and NaZSM-5-0.30.

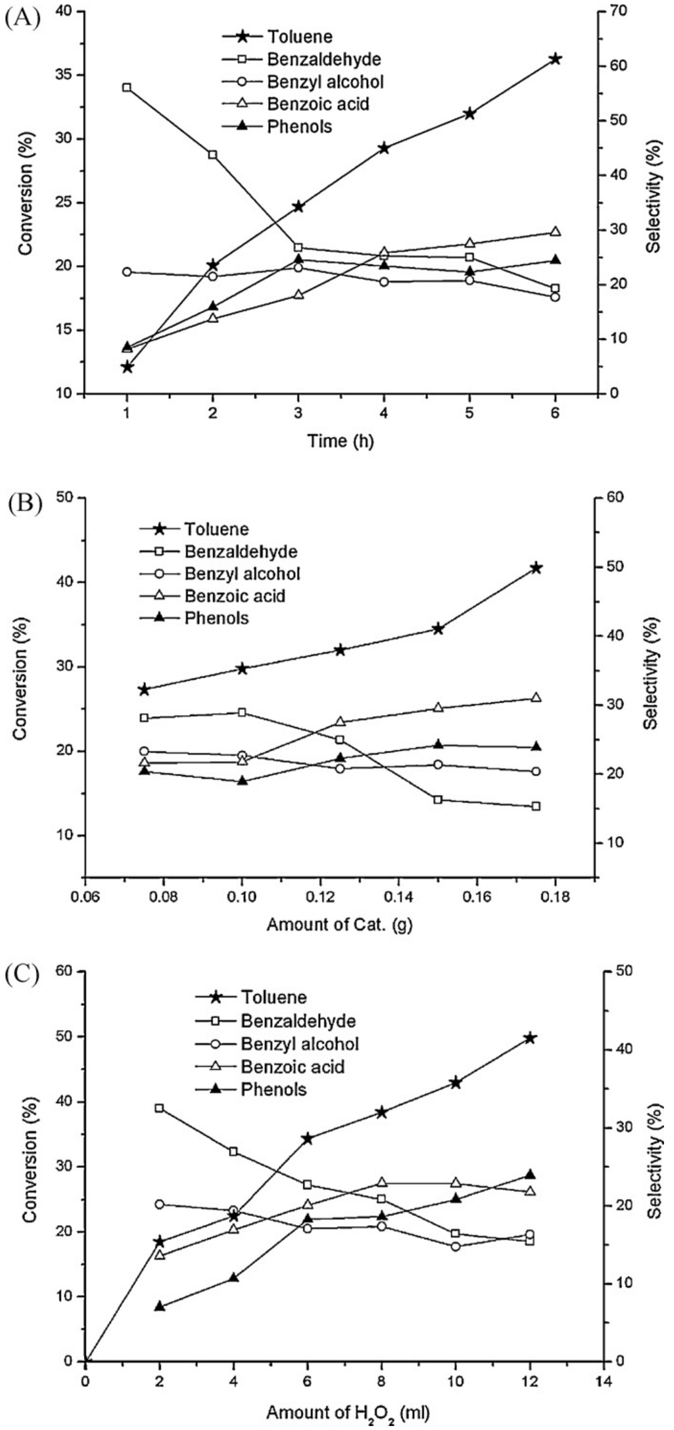

**Fig. 3.** (A) Effect of reaction time on conversion and selectivity of toluene oxidation catalyzed by HZSM-5-0.20. Reaction conditions: toluene (20.0 mmol), HZSM-5-0.20 (0.125 g), $H_2O$ (24.0 ml), $H_2O_2$ (8.0 ml), refluxing; (B) Effect of HZSM-5-0.20 amount on conversion and selectivity of toluene oxidation. Reaction conditions: toluene (20.0 mmol), $H_2O$ (24.0 ml), $H_2O_2$ (8.0 ml), refluxing for 5 h; (C) Effect of $H_2O_2$ amount on conversion and selectivity of toluene oxidation catalyzed by HZSM-5-0.20. Reaction conditions: toluene (20.0 mmol), HZSM-5-0.20 (0.125 g), $H_2O$ (24.0 ml), refluxing for 5 h.

conversion of toluene, suggesting that the amount of medium acid sites should be related to the catalytic oxidation activity. On the contrary, the HZSM-5 zeolites alkali-treated under severe condition gave relatively low conversion (9.5% by HZSM-5-0.40 and 18.1% by HZSM-5-0.30). The powder XRD profiles of HZSM-5-0.30 and HZSM-5-0.40 presented lower relative crystallinity than that of HZSM-5-0.20, implying that the reactivity for the oxidation of toluene depended on the amount of active sites in the framework. Either the production of benzaldehyde via the oxidation of benzyl alcohol or benzoic acid from benzaldehyde could be catalyzed by zeolites. Considering this fact, it was worthy to notice that the catalysts exhibited low conversion of toluene while high selectivity for benzaldehyde would be received. It suggested that the catalytic activity of alkali-treated zeolites for the oxidation of carbonyl compounds was weakened as the concentration of NaOH solution rose up from 0.20 to 0.40 mol/L. Among the alkali-treated NaZSM-5 zeolites, the highest conversion of toluene could be obtained by NaZSM-5-0.10. Compared with the relevant HZSM-5 zeolites, all of the alkali-treated NaZSM-5 samples exhibited lower selectivity for benzaldehyde and benzoic acid, but higher selectivity for phenols. To understand the high activity of HZSM-5-0.20, it was reasonable to suppose that the oxidation process of toluene could also be promoted by the consumption of benzyl alcohol and benzaldehyde in the formation of benzoic acid.

Fig. 3A displays the catalytic performance of HZSM-5-0.20 for toluene oxidation with different reaction times. In the first hour, the conversion of toluene could rapidly reach 12.1%, and finally 37.5% was obtained when the reaction time was prolonged to 6 h. The

**Table 2**
The performance of HZSM-5-0.20 for the oxidation of benzaldehyde, benzyl alcohol and esterification of benzyl alcohol with benzoic acid.

| Reaction | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|
| | | Benzaldehyde | Benzyl alcohol | Benzoic acid | Phenols |
| Benzaldehyde oxidation[a] | 95.6 | – | – | 92.9 | 3.2 |
| Benzyl alcohol oxidation[b] | 68.1 | 36.3 | – | 49.5 | 2.9 |
| Esterification[c] | <1 | – | – | – | – |

[a] Benzaldehyde (20.0 mmol), HZSM-5-0.20 (0.125 g), $H_2O_2$ (8.0 ml), distilled water (24.0 ml), refluxing for 3 h.
[b] Benzyl alcohol (20.0 mmol), HZSM-5-0.20 (0.125 g), $H_2O_2$ (8.0 ml), distilled water (24.0 ml), refluxing for 3 h.
[c] HZSM-5-0.20 (0.125 g), benzyl alcohol (20.0 mmol), benzoic acid (20.0 mmol), distilled water (24.0 ml), refluxing for 5 h.

effect of reaction time on the selectivity for the product showed the inherent feature of the oxidation in aqueous media. During the oxidative process of toluene, the selectivity for benzaldehyde continuously went down as the reaction time prolonging. According to these facts, benzaldehyde should be the primary product of toluene oxidation. Due to the oxidation of benzaldehyde with $H_2O_2$, benzaldehyde was transformed into benzoic acid. As a result, the selectivity for benzoic acid increased steadily as the reaction proceeded. If the yield of benzaldehyde was given the top priority, the reaction time should be no longer than 2 h. In this case, the oxidation by HZSM-5-0.20 gave about 45% selectivity for benzaldehyde and 20% toluene conversion. On the other hand, the oxidation of benzyl alcohol into benzaldehyde could be also carried out by alkali-treated zeolites with $H_2O_2$ (Table 2). Taking all of these facts into account, benzyl alcohol should be consumed as the reaction proceeds. In Fig. 3A, no obvious decrease in the selectivity for benzyl alcohol could be observed. It indicated that the rate for the production of benzyl alcohol via oxidation of toluene corresponded to the rate of consumption of benzyl alcohol in the oxidation. The benzyl alcohol was another primary product of toluene oxidation with $H_2O_2$ in aqueous media. The oxidation of toluene, benzaldehyde and benzyl alcohol should be catalyzed by zeolites in this system. Due to the further oxidation of primary products, the attempts intended to improve the conversion of toluene usually resulted in the high selectivity for benzoic acid along with the low selectivities for benzaldehyde and benzyl alcohol. As it has been discussed above, the enhancement of selectivities for benzaldehyde and benzyl alcohol with moderate conversion of toluene could be achieved through the choice of experiment conditions or different alkali-treated zeolites.

The amount of the catalyst used in the reaction was also checked as a function of the catalytic activity. The conversion of toluene continuously increased as the catalyst amount rose up, whereas the selectivity for benzaldehyde continuously decreased (Fig. 3B) and the selectivity for benzyl alcohol slightly decreased. This phenomenon suggested that the oxidation of toluene, benzaldehyde and benzyl alcohol might benefit from the increase of catalyst amount. Interestingly, the selectivity for benzoic acid varied synchronously with the toluene conversion which was induced by different amounts of HZSM-5-0.20 used in the reaction. Thus, benzoic acid could be the final products of oxidation in this system and be difficult to be further oxidized. Without hydrogen peroxide the oxidation of toluene could not occur in aqueous media under the presence of catalyst. The amount of oxidant used in the reaction was a key factor for the reactivity of toluene oxidation. The effect of $H_2O_2$ amount on the oxidation of toluene was investigated and the results are showed in Fig. 3C. Though higher toluene conversion could be obtained when the amount of $H_2O_2$ increased up to 10 ml, lower selectivities for benzaldehyde and benzyl alcohol were received. Thus, higher amount of $H_2O_2$ used in the reaction system would lead to higher reactivity of the oxidation of toluene, benzaldehyde and benzyl alcohol.

Besides the oxidation reactions, the esterification of benzyl alcohol with benzoic acid could also be catalyzed by the zeolites [33,34]. To promote the esterification, water as the main byproduct need to be removed from the reaction system. The ester had been frequently reported to be the main byproduct in liquid oxidation of toluene [35]. In order to restrict the production of esters, it was necessary to employ water as the sole medium in the process of oxidation. According to the results of esterification of benzyl alcohol with benzoic acid shown in Table 2, no esters could be detected when the reaction carried out in aqueous media for 5 h. The amount of water as the function of reactivity for the oxidation of toluene was checked and the results are listed in Table 3. When the $H_2O_2$ was directly added into the system, low toluene conversion and 75.2% of selectivity for the primary products (benzaldehyde, benzyl alcohol, benzoic acid and phenols) were obtained, whereas the byproducts took a great part of the products. The decomposition of $H_2O_2$ and the oxidation of toluene dramatically occurred without the employment of aqueous media. When water was used as solvent for the reaction, the selectivity for primary products obviously increased. The increment of water added into the system efficiently relaxed the decomposition of $H_2O_2$, thus resulting in the increase of conversion. But much more water would lead to the decrease of oxidative activity of $H_2O_2$, due to the diluted $H_2O_2$. The effect of reaction temperature on the oxidation of toluene was also studied. As Table 3 displays, when the temperature increased in the range from 20 to reflux temperature, the conversion of toluene

**Table 3**
The effect of reaction temperature and $H_2O$ amount on the oxidation of toluene.[a]

| Reaction temperature (°C) | $H_2O$ (ml) | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|---|
| | | | Benzaldehyde | Benzyl alcohol | Benzoic acid | Phenols |
| 20 | 24.0 | <1 | – | – | – | – |
| 40 | 24.0 | 7.3 | 61.9 | 23.6 | 6.6 | 3.5 |
| 60 | 24.0 | 10.2 | 57.5 | 23.0 | 10.9 | 4.3 |
| 70 | 24.0 | 17.4 | 47.4 | 23.3 | 11.7 | 11.3 |
| 80 | 24.0 | 27.1 | 29.1 | 20.9 | 19.4 | 22.5 |
| Refluxed[b] | – | 14.4 | 24.6 | 12.4 | 12.8 | 25.4 |
| Refluxed | 12.0 | 21.8 | 18.0 | 17.8 | 29.5 | 24.9 |
| Refluxed | 36.0 | 35.5 | 19.7 | 21.5 | 28.1 | 20.5 |
| Refluxed | 48.0 | 34.7 | 26.2 | 25.0 | 22.3 | 18.4 |

[a] Reaction conditions: HZSM-5-0.20 (0.125 g), toluene (20.0 mmol), $H_2O_2$ (8.0 ml), reaction time 5 h.
[b] The reaction temperature was at a range of 90–95 °C.

**Table 4**
Reusage of HZSM-5-0.20 for the oxidation of toluene.[a]

| RUN | Conversion (%) | Selectivity (%) | | | |
|---|---|---|---|---|---|
| | | Benzaldehyde | Benzyl alcohol | Benzoic acid | Phenols |
| 1 | 32.0 | 25.0 | 20.8 | 27.5 | 22.3 |
| 2 | 32.5 | 22.9 | 23.0 | 26.1 | 20.7 |
| 3 | 32.5 | 24.1 | 25.0 | 24.2 | 20.4 |
| 4 | 30.0 | 25.2 | 21.1 | 23.4 | 22.6 |
| 5 | 29.9 | 26.0 | 24.1 | 22.3 | 20.8 |
| 6 | 27.4 | 24.1 | 22.0 | 23.7 | 20.7 |

[a] Reaction conditions: HZSM-5-0.20 (0.125 g), toluene (20.0 mmol), $H_2O$ (24.0 ml), $H_2O_2$ (8.0 ml), refluxing for 5 h.

went up and the selectivity for the benzaldehyde decreased. The selectivities for benzoic acid and phenols varied synchronously with the toluene conversion. Thus, the oxidation of toluene and benzaldehyde could benefit from the increase of reaction temperature. Reusability studies with HZSM-5-0.20 resulted in about 5% loss in catalytic activity after 5 times' reusing (Table 4). Due to the fact that the catalytic activity of HZSM-5-0.20 became weaker in the recycling experiment, the selectivities for benzoic acid and phenols slightly decreased. The experiments indicated that HZSM-5-0.20 was a durable heterogeneous catalyst for toluene oxidation in aqueous media.

TS-1/$H_2O_2$ system had been reported to exhibit significant enhancement in the reaction rates for the hydroxylation of toluene in aqueous media comparing with anisole as solvent [30]. Though TS-1 showed well catalytic activity for the ring hydroxylation, the products which related to the side chain oxyfunctionalization had not been observed. In our work, zeolites (HZSM-5, NaZSM-5 and HBeta) could catalyze the side chain oxyfunctionalization of toluene forming benzaldehyde, benzyl alcohol and benzoic acid in aqueous media. Moreover, the catalytic performance of the zeolite could be significantly enhanced via the alkali-treatment. The alkali-treated zeolites exhibited high conversion of toluene with good selectivities toward benzaldehyde, benzyl alcohol and benzoic acid in only 5 h at a low temperature. And the alkali-treated zeolites were firstly used as heterogeneous catalysts for oxidation of toluene in aqueous media with $H_2O_2$.

Radical initiator had been proved to be necessary in some toluene oxidation system which was carried out in liquid phase under mild conditions [29]. Without any additive, in this work, toluene oxidation could be directly catalyzed by alkali-treated zeolites in aqueous media. Furthermore, no heavy metals or their oxides were considered in the synthesis of catalyst. This design of the catalyst avoids the release of heavy metal ions into the water and the consequent pollution. It is worthy to notice that the reaction was carried out in atmosphere at a low temperature. The mild reaction conditions avoid the formation of coke which usually leads to the inactivity of the catalyst. This is a key factor to determine the performance of heterogeneous catalyst in the recycling experiment. As it has been discussed above, the alkali-treated zeolites are able to be reused for 5 times in the oxidation of toluene without obvious decrease in the catalytic activity.

The $^{27}$Al MAS NMR spectra of HZSM-5-0.20 and NaZSM-5-0.10 are shown in Fig. 4. Strong peaks at 54 ppm assigned to tetrahedrally coordinated framework aluminum ($Al^{IV}$) could be observed in the spectra of samples. No signals could be detected at 0 ppm assigned to octahedrally coordinated extra-framework aluminum ($Al^{VI}$) [36–38]. Both of Si and Al atoms in MFI zeolites could be dissolved in the alkaline solution. The alkali-treatment of MFI zeolite resulted in the increase of the distorted Al atoms on the framework for the reason that more Si atoms than Al atoms were dissolved in the alkaline solution [39–42]. The species $\equiv Al^\bullet$ in the alkali-treated HZSM-5 and NaZSM-5 were mainly assigned to the distorted framework Al atoms formed by splitting Si–OH–Al groups. Except for the structural features, the acidity properties of MFI were determined by the Al atoms in the framework. As it has been supported by the results of $NH_3$-TPD, the amount of medium acid sites in zeolites would obviously increase via alkali-treatment of parent zeolites with alkaline solution of appropriate concentration. On the other hand, more Al atoms would be separated from the zeolite framework during the formation of oxides as the concentration of alkaline solution went up, leading to the weak catalytic activity (e.g. HZSM-5-0.40). It was reasonable to assume that the species $\equiv Al^\bullet$ could be related to the medium acid sites in zeolites, as well as the catalytic activity for the oxidation of toluene. Alkali-treatment also induced the formation of hydroxyl groups bonded to the distorted framework Al atoms ($\equiv$AlOH) via the splitting of Si–O–Al. And the amount of these hydroxyl groups was found to be related to the reactivity for the oxidation of benzaldehyde and benzyl alcohol [20,43,44]. Thus, the mechanism for toluene oxidation with $H_2O_2$ over the Al-containing alkali-treated zeolites could be proposed as shown in Fig. 5. The framework aluminum directly catalyzed the oxidation of toluene into benzaldehyde, benzyl alcohol and benzoic acid. As shown in formula 1, the distorted framework Al atoms could activate $H_2O_2$ molecule, that is, the species $\equiv Al^\bullet$ reacts with $H_2O_2$ proceeding with the formation of $\equiv Al(H_2O_2)$. The methyl group in toluene molecule was oxidized by $\equiv Al(H_2O_2)$, resulting in the formation of benzyl alcohol. The activated $H_2O_2$ could also

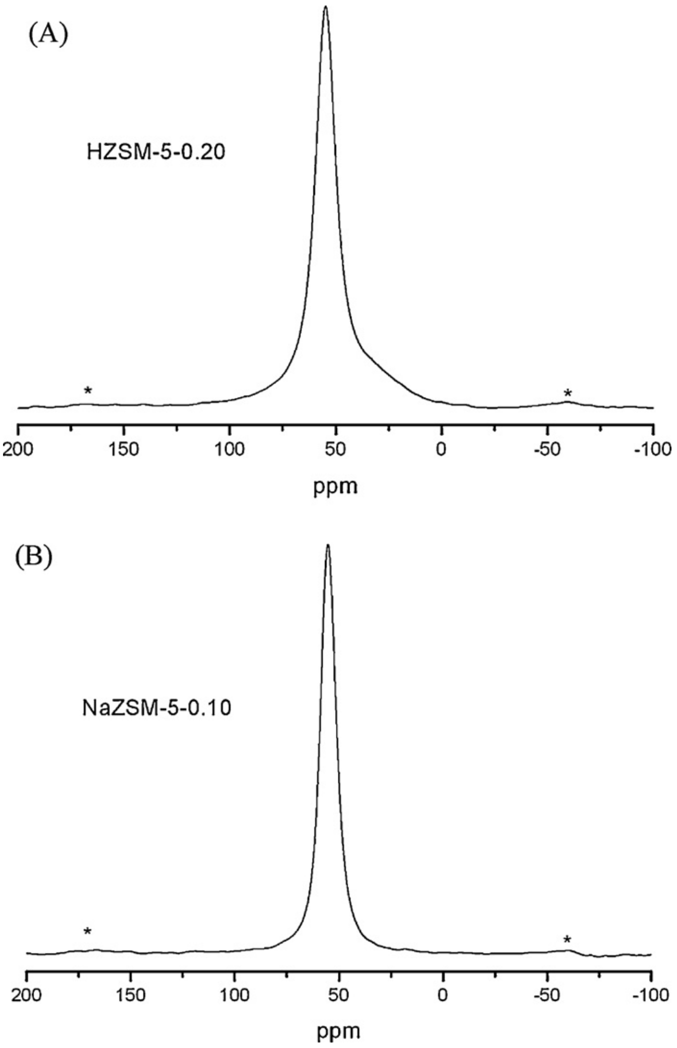

**Fig. 4.** $^{27}$Al MAS NMR spectra of (A) HZSM-5-0.20 and (B) NaZSM-5-0.10.

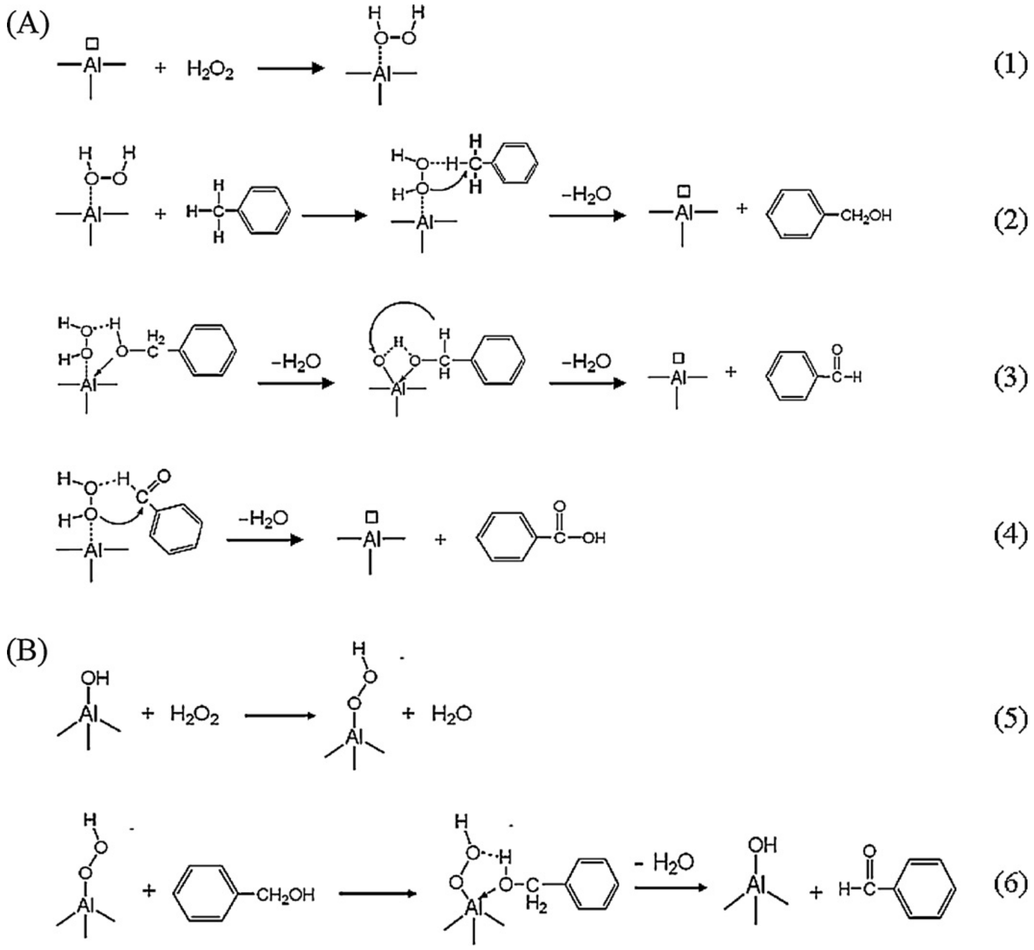

**Fig. 5.** Schematic illustration of the mechanism for the toluene oxidation with $H_2O_2$.

oxidize benzyl alcohol to yield benzaldehyde. The further oxidation of benzaldehyde resulted in the formation of benzoic acid. Furthermore, the oxidation of benzyl alcohol and benzaldehyde could be also catalyzed by the species ≡AlOH (Fig. 5B), which can react with $H_2O_2$ to yield the aluminum complex AlOOH. In the following process, AlOOH would react with benzaldehyde and benzyl alcohol to produce benzoic acid and benzaldehyde, respectively. As it has been mentioned above, the oxidation process of toluene could be promoted by the consumption of benzyl alcohol and benzaldehyde. Thus, the species ≡AlOH played an important role in the oxidation of toluene. The difference in the catalytic performance of alkali-treated HZSM-5 and NaZSM-5 might be related to the amount of species ≡AlOH and ≡Al$^{\bullet}$ in the zeolites. The catalytic reactivity of alkali-treated HZSM-5 and NaZSM-5 zeolites for the oxidation of toluene could be related to the structural defects in zeolites.

## 4. Conclusions

In this work, it was found that alkali-treated zeolites could efficiently catalyze oxidation of toluene with $H_2O_2$ in aqueous media. Here series of alkali-treated zeolites were firstly used as heterogeneous catalysts for liquid-phase oxidation of toluene with $H_2O_2$. The liquid-phase oxidation of toluene with 8.0 ml hydrogen peroxide catalyzed by 0.125 g HZSM-5-0.20 gave 32.0% conversion with selective formation of 25.0% benzaldehyde, 20.8% benzyl alcohol, 27.5% benzoic acid and 22.3% phenols. The absence of additive and heavy metals determined that the catalytic system is simple and environmental-friendly. Furthermore, the mild reaction conditions avoided the formation of coke on the catalyst. And the results of recycling experiment demonstrated that alkali-treated HZSM-5 zeolite was a durable heterogeneous catalyst for the liquid-phase oxidation of toluene. In conclusion, this catalytic system enriches the common processes of toluene oxidation and further investigation based on these preliminary results might introduce new insight into the catalytic mechanism of toluene oxidation. Moreover, alkali-treated zeolites are promising catalysts for the oxidation of toluene in the industrial application.

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## References

[1] S. Minakata, M. Komatsu, Chem. Rev. 109 (2009) 711–724.
[2] M. Eissen, J.O. Metzger, E. Schmidt, U. Schneidewind, Angew. Chem. Int. Ed. 41 (2002) 414–436.
[3] S. Narayan, J. Muldoon, M.G. Finn, V.V. Fokin, H.C. Kolb, K.B. Sharpless, Angew. Chem. Int. Ed. 44 (2005) 3275–3279.
[4] U.M. Lindstrom, Chem. Rev. 102 (2002) 2751–2772.
[5] C.J. Li, Chem. Rev. 105 (2005) 3095–3166.
[6] J.J. Gajewski, Acc. Chem. Res. 30 (1997) 219–225.
[7] W. Lu, T.H. Chan, J. Org. Chem. 66 (2001) 3467–3473.
[8] V.V. Fokin, K.B. Sharpless, Angew. Chem. Int. Ed. 40 (2001) 3455–3457.
[9] S. Kobayashi, K. Manabe, Acc. Chem. Res. 35 (2002) 209–217.
[10] S. Tascioglu, Tetrahedron 52 (1996) 11113–11152.

[11] K. Manabe, Y. Mori, T. Wakabayashi, S. Nagayama, S. Kobayashi, J. Am. Chem. Soc. 122 (2000) 7202–7207.
[12] R. Breslow, C.J. Rizzo, J. Am. Chem. Soc. 113 (1991) 4340–4341.
[13] K. Itami, T. Nokami, J.I. Yoshida, Angew. Chem. Int. Ed. 40 (2001) 1074–1076.
[14] S. Nagayama, S. Kobayashi, Angew. Chem. Int. Ed. 39 (2000) 567–569.
[15] S. Kobayashi, K. Manabe, Chem. Eur. J. 8 (2002) 4094–4101.
[16] Y. Uozumi, K. Shibatomi, J. Am. Chem. Soc. 123 (2001) 2919–2920.
[17] G. Sartori, F. Bigi, R. Maggi, A. Mazzacani, G. Oppici, Eur. J. Org. Chem. (2001) 2513–2518.
[18] S. Kobayashi, Eur. J. Org. Chem. (1999) 15–27.
[19] P. Sreekanth, S.W. Kim, T. Hyeon, B.M. Kim, Adv. Synth. Catal. 345 (2003) 936–938.
[20] A. Jia, L.-L. Lou, C. Zhang, Y. Zhang, S. Liu, J. Mol. Catal. A: Chem. 306 (2009) 123–129.
[21] A.P. Antunes, M.F. Ribeiro, J.M. Silva, F.R. Ribeiro, P. Magnoux, M. Guisnet, Appl. Catal. B: Environ. 33 (2001) 149–164.
[22] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037–3058.
[23] Ch. Subrahmanyam, B. Louis, T.K. Varadarajan, B. Viswanathan, A. Renken, Appl. Catal. A: Gen. 282 (2005) 67–71.
[24] F.M. Bautista, J.M. Campelo, D. Luna, J. Luque, J.M. Marinas, Appl. Catal. A: Gen. 325 (2007) 336–344.
[25] J. Carpentier, J.F. Lamonier, S. Siffert, E.A. Zhilinskaya, A. Aboukais, Appl. Catal. A: Gen. 234 (2002) 91–101.
[26] L. Matachowski, K. Pamin, J. Poltowicz, E.M. Serwicka, W. Jones, R. Mokaya, Appl. Catal. A: Gen. 313 (2006) 106–111.
[27] V.R. Rani, M.R. Kishan, S.J. Kulkarni, K.V. Raghavan, Catal. Commun. 6 (2005) 531–538.
[28] F. Yang, J. Sun, R. Zheng, W. Qiu, J. Tang, M. He, Tetrahedron 60 (2004) 1225–1228.
[29] L. Kesavan, R. Tiruvalam, M.H. Ab Rahim, M.I. bin Saiman, D.I. Enache, R.L. Jenkins, N. Dimitratos, J.A. Lopez-Sanchez, S.H. Taylor, D.W. Knight, C.J. Kiely, G.J. Hutchings, Science 331 (2011) 195–199.
[30] R. Kumar, A. Bhaumik, Microporous Mesoporous Mater. 21 (1998) 497–504.
[31] K. Liu, S. Xie, G. Xu, Y. Li, S. Liu, L. Xu, Appl. Catal. A: Gen. 383 (2010) 102–111.
[32] J.H. Kim, M.J. Park, S.J. Kim, O.S. Joo, K.D. Jung, Appl. Catal. A: Gen. 264 (2004) 37–41.
[33] M. Xu, J.H. Lunsford, D.W. Goodman, A. Bhattacharyya, Appl. Catal. A: Gen. 149 (1997) 289–301.
[34] N. Viswanadham, R. Kamble, M. Singh, M. Kumar, G.M. Dhar, Catal. Today 141 (2009) 182–186.
[35] Y. Zhang, C. Li, X. He, B. Chen, Chin. J. Chem. Eng. 16 (2008) 36–38.
[36] Y. Fan, X.J. Bao, X.Y. Lin, G. Shi, H.Y. Liu, J. Phys. Chem. B 110 (2006) 15411–15416.
[37] N. Xue, R. Olindo, J.A. Lercher, J. Phys. Chem. C 114 (2010) 15763–15770.
[38] H. Wang, L. Su, J. Zhuang, D. Tan, Y. Xu, X. Bao, J. Phys. Chem. B 107 (2003) 12964–12972.
[39] O. Bortnovsky, Z. Sobalik, B. Wichterlova, Z. Bastl, J. Catal. 210 (2002) 171–182.
[40] J.S. Jung, J.W. Park, G. Seo, Appl. Catal. A: Gen. 288 (2005) 149–157.
[41] D.H. Choi, J.W. Park, J.H. Kim, Y. Sugi, G. Seo, Polym. Degrad. Stab. 91 (2006) 2860–2866.
[42] K. Barbera, F. Bonino, S. Bordiga, T.V.W. Janssens, P. Beato, J. Catal. 280 (2011) 196–205.
[43] M.P. Chaudhari, S.B. Sawant, Chem. Eng. J. 106 (2005) 111–118.
[44] S. Endud, K.L. Wong, Microporous Mesoporous Mater. 101 (2007) 256–263.