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New Process of 2-Nitrotoluene into 2-Methylaniline by Transfer Hydrogenation with Methanol over X Zeolite Catalyst

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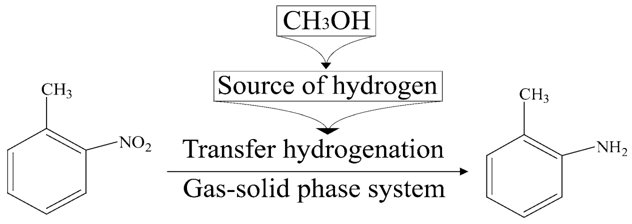
Abstract A new transfer hydrogenation of 2-nitrotoluene with methanol to 2-methylaniline was successfully implemented. The transfer hydrogenation of 2-nitrotoluene with methanol showed much faster rate than its hydrogenation with hydrogen over X zeolites. Based on the reaction results over different modified X zeolites and activated carbon, a radical mechanism was proposed.

Graphical Abstract



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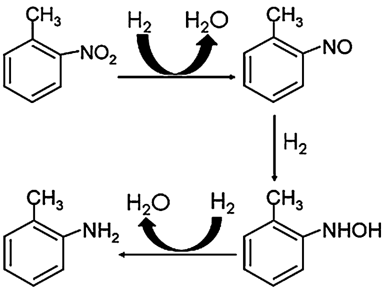
Keywords Transfer hydrogenation · Methanol · X zeolite · 2-Nitrotoluene · 2-Methylaniline

1 Introduction

As a very important organic intermediate, 2-methylaniline is a widely used precursor to synthesize many useful chemical materials, such as pesticides, medicines, and dyestuffs, etc. Commonly, 2-methylaniline is produced by the process of liquid-phase hydrogenation of 2-nitrotoluene under high pressures in the tank reactor due to the relatively higher boiling point of 2-nitrotoluene as shown below.



However, these production processes always consume a large amount of hydrogen and need the separation of solvent, being lower production efficiency, expensive equipment and higher energy consumption. More importantly, the catalysts for liquid-phase hydrogenation, like Pt/Pd-type catalysts, are very expensive and often could not be able to recycle. Therefore, it is desirable to explore a high-efficiency, more economic and environment-friendly reaction route and inexpensive catalysts.

Although catalytic hydrogenation is an environmental friendly method for the reduction of aromatic nitro compounds, it has some difficulties in safety. With the development of green chemistry, many hydrogenation processes can be realized by catalytic transfer hydrogenation (CTH)

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using molecules containing hydrogen atoms other than molecular hydrogen as the source of hydrogen [1–4]. Compared with the traditional hydrogenation process, CTH possesses the advantage of high safety, low equipment requirement. At present, existing transfer hydrogenation generally requires the participation of noble metals, such as Ru, Pt, Pd, Ir etc. [5–10]. However, these metal catalysts or metal-supported catalysts often accompany with the loss of active components, which causing a short life and a high catalyst cost. Furthermore, the reduction of nitroarenes to aromatic amines needs to be provided a liquid environment for the system and a longer reaction time. Therefore, the transfer hydrogenation is always limited by the solvent to a large extent. The kind of solvent, amount of solvent, and contact time have significantly effect on the reaction results. Meanwhile, the use of solvents likely to cause a larger amount of wastes.

In this work, we successfully complete the process of the transfer hydrogenation of 2-nitrotoluene to 2-methylaniline with a new facile approach to use methanol as hydrogen resource. This new process carried out in a gas–solid phase reaction system at a fixed bed reactor over non-noble metal X zeolite as a hydrogenation catalysts. Obviously, this continuous production process is no need to separate the catalysts from the solvents, which improving the production efficiency and simplifying the production process.

2 Experimental

2.1 Catalyst Preparation

The Na-X (Tongxing zeolite industry, Shanghai, Si/Al = 1.27) was ion-exchanged with NH_4^+, K^+, Cs^+ to prepare NH_4-type X, KX, CsX, respectively. CsOH was used as a source of Cs^+, NH_4Cl and $KHCO_3$ were used as the sources of NH_4^+ and K^+, respectively. An aqueous solution of CsOH (400 mL, 0.75 M) and NaX (20 g) were mixed, stirred for 5 min and kept for 4 h at 363 K. The slurry was filtered with Buchner funnel. The filtered cake was dried in an oven at 373 K for 12 h and calcined at 793 K for 4 h in a muffle furnace in air. The sample was again immersed in an aqueous solution of CsOH (400 mL, 0.75 M), stirred and kept for 4 h at 363 K. The above procedures were repeated for two more times (total ion-exchange for three times). The obtained catalyst was pressed, crushed, and sorted to get parent CsX catalysts (particles of 12–20 mush, donated as CsX). KX and NH_4-type X were prepared by following the same method, replacing the precursor solution with 1.0 mol/L $KHCO_3$ and 1.0 mol/L NH_4Cl, respectively. NH_4-type X was calcined at 793 K for 2 h with a rate of 3 K/min to obtain H-type X, donated as HX.

The characterizations of the modified X zeolites are shown in the supplemental file. The X-ray diffraction patterns of catalysts were recorded on a BRUKER D8 ADVANCE diffractometer using Cu Kα radiation, which was operated at 40 kV and 40 mA. A scanning rate of 5 °/min was used for Bragg's angles $2\theta = 5$–50°. The specific surface area of catalysts was determined by nitrogen adsorption at 77 K on a Quantachrome Nova-2200e sorptometer and calculated by the Brunauer–Emmett–Teller (BET) method. Samples were pre-treated at 573 K for 3 h in a vacuum prior to the measurement. The elemental compositions of catalysts were determined by inductively coupled plasma (ICP, OPTIMA2100DV, Perkin Elmer). The acidity of catalysts was determined by pyridine-infrared spectroscopy (Py-IR) (Bruker IFS-88). The basicity of catalysts was determined by test reaction of the alkylation of toluene with methanol and characterized by IR with phenol adsorption. The test reaction conditions were as follows: reaction temperature 703 K, Toluene/Methanol molar ratio of 5, WHSV of 1.0 h^{-1}, with nitrogen as carrier gas at atmosphere pressure. TG curves were measured with a NETZSCH STA449C for the uncalcined samples, with α-Al_2O_3 being used as a reference sample. The sample was heated at a rate of 10 K/min in a static air.

2.2 Reaction Procedures

A fixed bed tubular reactor system was employed for carrying out three type reactions, i.e., 2-nitrotoluene react with methanol, 2-nitrotoluene react with formaldehyde and hydrogenation of 2-nitrotoluene with H_2. The specific reaction conditions as follows: reaction temperature of 718 K, weight hourly space velocity (WHSV) of 1.0 h^{-1}, atmospheric pressure. A catalyst sample (5 g) was packed into a stainless steel with 1.5 cm inner diameter (50 cm length) and pretreated in a flowing N_2 at 718 K for 1 h prior to the reaction. For the reaction of 2-nitrotoluene with methanol, the mixture containing 1:1 molar ratio of 2-nitrotoluene to methanol was pumped into the reactor at the rate of 0.11 mL/min by a metering pump. The raw material was replaced with 2-nitrotoluene and formaldehyde in 1:1 molar ratio for the reaction of 2-nitrotoluene with formaldehyde. These reactions were all conducted under the N_2 flow of 40 mL/min with atmospheric pressure. For hydrogenation of 2-nitrotoluene, 2-nitrotoluene was fed into the reactor at the rate of 0.11 mL/min with a H_2 flow of 40 mL/min. The reactor effluent was analyzed with online gas chromatograph HP-5890 equipped with a FID detector and a 50 m HP-FFAP capillary column.

3 Results and Discussion

3.1 Reaction of 2-Nitrotoluene with Methanol

In the reaction of 2-nitrotoluene with methanol over KX at a fixed bed reactor, the product of reduction of 2-nitrotoluene, 2-methylaniline, was found as shown in Fig. 1. Other by-products as being detected in the reduction of 2-nitrotoluene with hydrogen, such as toluene, aniline, also were formed in the reaction of 2-nitrotoluene with methanol. The highest conversion of 2-nitrotoluene and selectivity of 2-methylaniline were 73.09 and 58.19 %, respectively. However, nitrostyrene and nitroethylbenzene which might be formed as the products of the side-chain alkylation of 2-nitrotoluene with methanol as the alkylating reagents were not produced. The conversion of 2-nitrotoluene slighted decreased after 4 h. The catalytic performance of KX decreased obviously after 8 h, and the catalysts became deep black. From the characterization of TG (as shown in Figure S4) and the experiments of the transfer hydrogenation of 2-nitrotoulene with methanol over regenerated X zeolite (as shown in Table S5), the deactivation of catalysts was mainly due to coke deposition.

3.2 Reactions of 2-Nitrotoluene with Hydrogen, Formaldehyde and Methanol

Methanol reaction over alkali exchanged FAU(X) molecular sieves yielded surface formaldehyde, which was found to decompose into CO and H_2 [11, 12]. So the reaction process of 2-nitrotoluene with methanol over KX zeolite might be performed by three pathways. Firstly, 2-methylaniline was formed by the transfer hydrogenation of 2-nitrotoluene with methanol (the source of hydrogen). Secondly, methanol interacted with basic zeolite and converted into formaldehyde, then KX catalyzed the reaction of formaldehyde with 2-nitrotoluene to 2-methylaniline. Thirdly, 2-nitrotoluene reacted with hydrogen which was originated in the decomposition of methanol.

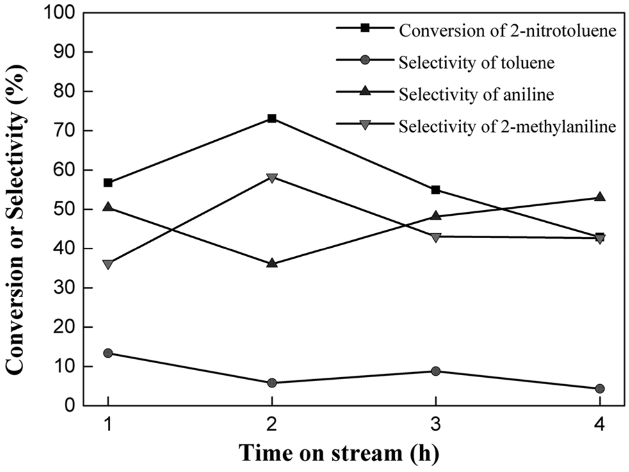

Fig. 1 Reaction of 2-nitrotoluene with methanol over KX zeolite. Reaction conditions: 718 K, WHSV of 1.0 h^{-1}, molar ratio of 2-nitrotoluene/methanol of 1.0, N_2 flow rates of 40 mL/min, atmosphere pressure

Figure 2 shows the product distribution of the reactions of 2-nitrotoluene with hydrogen, formaldehyde and methanol over KX, respectively. In the same conditions, the conversion of 2-nitrotoluene and the selectivity of 2-methylaniline of hydrogenation with H_2 (7.38, 27.64 %) and reaction with formaldehyde (5.78, 43.78 %) were much lower than the transfer hydrogenation (73.09, 58.19 %) over KX zeolite. Therefore, the transfer hydrogenation of 2-nitrotoluene with methanol proceeded significantly faster than the hydrogenation of 2-nitrotoluene with hydrogen and the reaction with formaldehyde for KX zeolite. The hydrogenation of 2-nitrotoluene and the transfer hydrogenation with formaldehyde were so slow to be excluded from the higher conversion of 2-nitrotoluene. Comparatively, when 2-nitrotoluene reacted with methanol under hydrogen atmosphere, the conversion of 2-nitrotoluene (from 73.09 to 74.83 %) and the selectivity of aniline (from 36.02 to 39.13 %) and 2-methylaniline (from 58.19 to 54.58 %) have no significant change over KX, as shown in Table 1.

From the above, it could concluded that 2-methylaniline was mainly formed by the transfer hydrogenation of 2-nitrotoluene with methanol over KX zeolite.

3.3 Transfer Hydrogenation over Different Modified X Zeolites

Different kinds of X zeolites modified by ion-exchange were applied to the reaction of transfer hydrogenation, the reaction results are shown in Table 2. For all catalysts, the

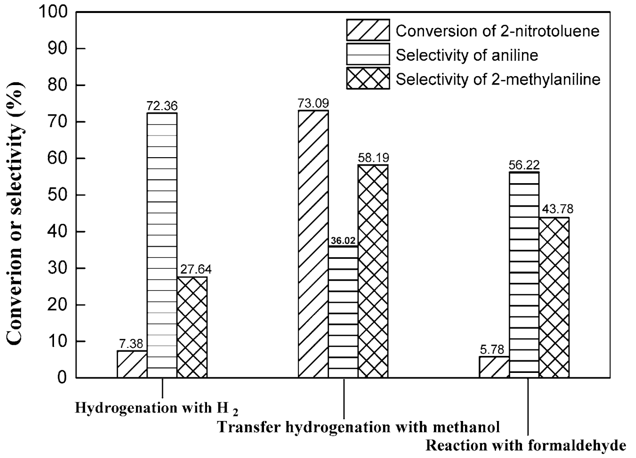

Fig. 2 Reactions of 2-nitrotoluene with hydrogen, methanol and formaldehyde over KX zeolite

Table 1 KX catalyze the reaction of 2-nitrotoluene with methanol under N_2 and H_2

Atmosphere	Conversion (%)		Selectivity (%)		
	2-Nitrotoluene	Methanol	Toluene	Aniline	2-Methylaniline
N_2	73.09	49.71	5.79	36.02	58.19
H_2	74.83	60.45	6.21	39.13	54.58

The detailed calculation equation of the conversion and selectivity is shown in the supplementary material (with page 1, Mass balance obtained)

distribution of product did not change obviously, and different catalysts mainly affected the conversion of 2-nitrotoluene and methanol. Transfer hydrogenation achieved the highest conversion of 2-nitrotoluene (76.70 %) over NaX, and the highest yield of main product 2-methylaniline (42.53 %) over KX. As an acid zeolite, HX possessed a distinctly different chemical properties according to the classification of acid or basic zeolite. However, the reaction of the transfer hydrogenation did not exhibited the similar difference over HX. Although the conversion of 2-nitrotoluene over HX was lower than other X zeolites, the distribution of products was similar, the selectivity of toluene, aniline, 2-methylaniline was 5.75, 42.37, 51.88 %, respectively. From the above, X zeolites with various acidity and alkalinity exhibited a similar tendency for the transfer hydrogenation, high conversion of 2-nitrotoluene and the selectivity of 2-methylaniline around 50 %. The perceptible differences between four types of X zeolites were the different conversion of 2-nitrotoluene and the different utilization of methanol. These indicated that acidity or alkalinity on X zeolite was not the main interaction factor for the transfer hydrogenation. When activated carbon was applied to catalyze the reaction of 2-nitrotoluene with methanol, the same products as transfer hydrogenation over X zeolites were obtained, although the catalytic activity and selectivity was much lower than X zeolites (14.98, 29.29 %). However, when the reaction was carried out in in the empty stainless steel reactor, toluene and aniline were the main products because of the de-methyl group and de-nitro group. The selectivity of 2-methylaniline was only 5.49 %.

3.4 The Mechanism of Transfer Hydrogenation of 2-Nitrotoluene with Methanol

The mechanism of side chain alkylation of toluene with methanol to styrene, over X zeolites exchanged with alkali-cation, postulated by Itoh et al. [13] was widely accepted, as shown in Fig. 3. Generally, as a stronger electron-withdrawing group, nitro could facilitate the polarization of the methyl C-H on the aromatic ring to a negatively charged methyl carbon to form the products of the side chain alkylation. Moreover, the methyl hydrogen from NO_2-Ph-CH_3 ($pKa = 20.4$) is easier to dissociate into H^+ than that of toluene ($pKa = 43$), and p-nitro-benzyl anion (NO_2–Ph–CH_2^-) is more stable than benzyl anion (Ph–CH_2^-). If the transfer hydrogenation of 2-nitrotoluene with methanol follows the similar ion mechanism, the side-chain alkylation products are easier to form than the reaction of side-chain alkylation of toluene with methanol. However, under the same reaction conditions, there were no nitrostyrene and nitroethylbenzene formation in the reaction of 2-nitrotoluene with methanol.

When the transfer hydrogenation reaction is interpreted by other kinds of ion mechanism, the donor of hydrogen-H^+ is needed. It is easy to understand that methanol converts to H^+ and $^-CH_2OH$ on the base sites of basic zeolites (such as KX and CsX), as shown in Fig. 4. The stronger alkalinity, the easier formation of H^+. But it scarcely occurs on the acid zeolite, HX and activated carbon. Normally, the alkalinity of CsX zeolite is stronger than KX and NaX, it prefers to the formation of H^+. At the same reaction conditions, the conversion of methanol in the side-

Table 2 Transfer hydrogenation of 2-nitrotoluene with methanol over different modified X zeolites

Catalyst	Conversion (%)		Selectivity (%)		
	2-Nitrotoluene	Methanol	Toluene	Aniline	2-Methylaniline
NaX	76.70	72.39	6.71	46.74	46.54
KX	73.09	49.71	5.79	36.02	58.19
CsX	63.97	79.83	6.25	44.51	49.24
HX	55.63	95.43	5.75	42.37	51.88
Activated carbon	14.98	52.56	19.70	51.01	29.29
None	10.14	49.86	79.92	14.59	5.49

The detailed calculation equation of the conversion and selectivity is shown in the supplementary material (with page 1, Mass balance obtained)

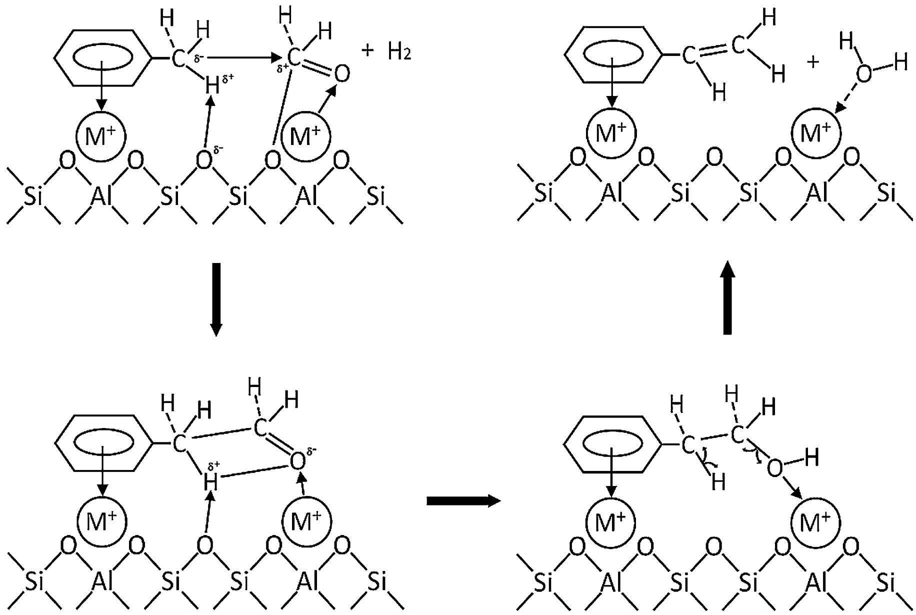

Fig. 3 The mechanism of side chain alkylation of toluene with methanol to styrene

chain alkylation of toluene with methanol over KX and CsX zeolites was almost 100 %. However, the conversion of methanol in the reactive system of transfer hydrogenation over X zeolite was less than 80 %, as shown in Table 2. If the formed H^+ participates in the transfer hydrogenation process, it could not explain the lower catalytic performance of CsX than KX and NaX in the transfer hydrogenation of 2-nitrotoluene with methanol under the premise of not completely decomposed in methanol. Besides, the catalytic activity of HX and activated carbon for the transfer hydrogenation in an ionization mechanism was impracticable.

According to the report results in the preceding paper, the side chain alkylation of toluene with methanol to styrene might be conducted with a radical mechanism, which has been validated by many experiments and characteristic methods (Chinese Journal of Catalysis, in press). According to the reactive performance over the activated carbon and different modified X zeolites, it seems that the transfer hydrogenation of 2-nitrotoluene with methanol also can be interpreted by the radical mechanism reasonably. However, the common methods, such as the spin trapping-electron spin resonance (ESR) technique, are hard to prove that the transfer hydrogenation of 2-nitrotoluene with methanol complies with free radical mechanism because the radical trapper cannot be used at the higher reaction temperature (718 K). Therefore, there was no visualized scientific evidence to prove the existence of radicals in the process of transfer hydrogenation of 2-nitrotoluene with methanol. Even so, some of the phenomenon cannot be ignored. Nitro radicals from 2-nitrotoluene and hydrogen radicals from methanol are relatively easy to form at the high reaction temperature. And the nitroarenes are typical free radical scavenger because nitro-group can react with active radicals to form more stable radicals. From the above, a possible mechanism with radical was predicted for the transfer hydrogenation of 2-nitrotoluene with methanol, as shown in Fig. 5.

The formation of hydrogen radicals was the prerequisite to the accomplishment of free radical process. Nitro-group reacted with the active hydrogen radical to stabilize the active free radicals and form the objective product 2-methylaniline eventually. Compared to the activated carbon, X-type zeolites exhibit better catalytic performance. It is probably due to the captodative effect among

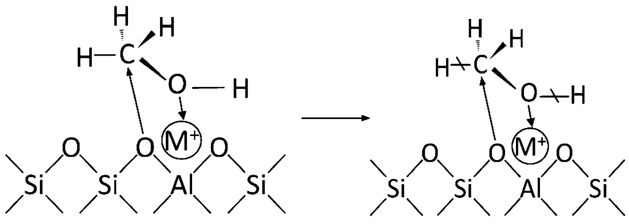

Fig. 4 Methanol reaction over basic X zeolites

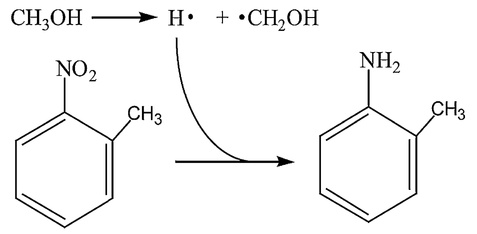

Fig. 5 The radical mechanism of transfer hydrogenation of 2-nitrotouene with methanol

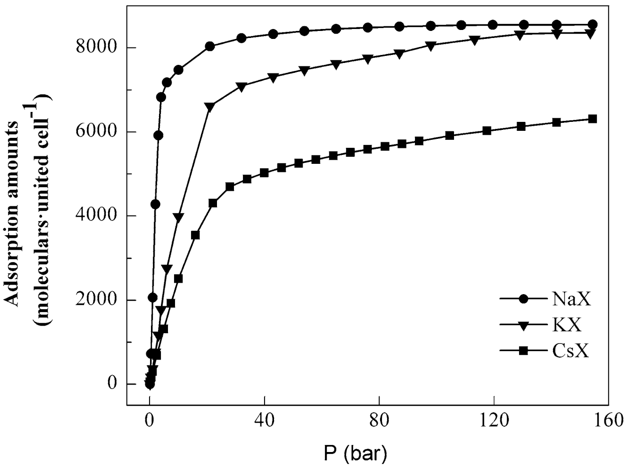

Fig. 6 Adsorption isotherms of methanol on X zeolites

the X zeolites. When an electron-withdrawing (captor) and an electron-releasing (donor) attach to the sides of a radical center, it would greatly increase the stability of the free radical. When the 2-nitrotoluene entered into X zeolites, it was stronger adsorbed on the extra framework cations of zeolites due to the interactions between the 2-nitrotoluene π-electrons (electron pair donor) with the cation (electron pair acceptor). The interactions between electron-withdrawing of the aromatic ring and pushing electron of methyl, the anion on the framework of zeolite donates the electron to nitro group of 2-nitrotoluene. Therefore, the X zeolite can stabilize CH_3–Ph–NO_2·, which is beneficial to the reaction process of free radicals. From Table 2, the catalytic performance for transfer hydrogenation of 2-nitrotoluene with methanol over NaX and KX were better than CsX. This probably attributes to the larger adsorption capacity of methanol over NaX and KX than that over CsX. The adsorption isotherms for CH_3OH were measured and the obtained results are shown in Fig. 6. NaX has similar adsorption capacity (ca. 8500 molecules · unit cell^{-1}) to KX. The adsorption capacity of methanol over NaX and KX are significantly larger than that over CsX (ca. 6300 molecules unit cell^{-1}). On the other hand, methanol over HX produce more dimethyl ether, while CsX produce more CO and H_2 [14]. Therefore, the conversion of methanol over HX and CsX are higher than that over NaX and KX. Like X molecular sieve, the activated carbon has a large specific surface area and a certain channel environment, which is beneficial to the adsorption of 2-nitrotoluene and methanol and the reactive collision, thus more conductive to the transfer hydrogenation reactions than that without any catalyst.

4 Conclusions

The reaction of 2-nitrotoluene with methanol to 2-methylaniline was proved to the process of transfer hydrogenation. As a new way to prepare 2-methylaniline, X zeolites exhibited the higher catalytic performance for the transfer hydrogenation of 2-nitrotoluene with methanol, especially for KX. In comparison to the different catalytic performance over activated carbon and different acid or basic X zeolites, it is reasonable to interpret this phenomenon in the radical mechanism.

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