Cu–H-MCM-41, H-MCM-41 and Na-MCM-41 mesoporous molecular sieve catalysts for isomerization of 1-butene to isobutene

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Cu–H-MCM-41, H-MCM-41 and Na-MCM-41 mesoporous molecular sieve catalysts were synthesized, characterized and investigated in the isomerization of 1-butene to isobutene. Introduction of copper in MCM-41 was found to play a positive role in enhancing the conversion of 1-butene and yield of isobutene and Cu–H-MCM-41 exhibited higher conversion of 1-butene and yield to isobutene than H-MCM-41 and Na-MCM-41 catalysts. The pretreatments of Cu–H-MCM-41 catalyst with synthetic air or hydrogen were observed to influence the 1-butene conversion, yield of isobutene and selectivity to isobutene. Pre-treated with the synthetic air the Cu–H-MCM-41-Ox catalyst exhibited higher conversion of 1-butene, yield of isobutene and selectivity to isobutene than hydrogen pre-treated Cu–H-MCM-41-Red. The reason for such a behavior of Cu–H-MCM-41-Red is the reduction of copper species to metallic form. The X-ray powder diffraction pattern of Cu–H-MCM-41-Red exhibited a peak attributed to the reduction of Cu^{2+} to Cu^0. FTIR spectra of adsorbed pyridine showed the presence of Brønsted and Lewis acid sites in the H-MCM-41, Na-MCM-41 and Cu–H-MCM-41 catalysts.

KEY WORDS: 1-butene; isomerization; MCM-41; mesoporous; catalysts; copper

1. Introduction

Isomerization of *n*-butenes to isobutene has attracted the attention of researchers in industry and academia, because isobutene is used as one of the starting raw materials in the synthesis of MTBE, an octane booster additive to gasoline. Isobutene is also used in the production of butyl rubber. Several proton form zeolite catalysts such as ZSM-22, Na-ZSM-35/FER, ZSM-5 and SAPO-11 have been investigated in the skeletal isomerization of 1-butene to isobutene [1–5]. The structure, pore size, shape selective and acidic property of zeolites are important parameters influencing the conversion of 1-butene and yield of isobutene [6,7]. The most promising catalysts were proton form zeolites with 10 membered rings having shape selective property. The investigations regarding cation (copper, nickel, cobalt and magnesium) modified zeolites and mesoporous molecular sieves in the isomerization of 1-butene have not been reported in the open literature. There is only one patent, which describes the application of cation-exchanged zeolites in the isomerization of 1-butene to isobutene [8].

MCM-41 is a new inorganic mesoporous material with very high surface area, mild acidity and hexagonal array of cylindrical pores [9–11]. The mesoporous material can be synthesized with pore diameters from 15 to 100 Å. There are several publications regarding the application of acid- and metal-modified MCM-41 in the reactions of fine chemicals, hydrocracking of gasoil and environmental catalysis [12–16]. Isomerization of 1-butene to isobutene has been reported over proton form mesoporous materials [17]. However, there are no reports in the literature on the investigation of isomerization of 1-butene over Cu-modified MCM-41 catalysts. The aim of this work was to synthesize and characterize Na-MCM-41, H-MCM-41 and Cu–H-MCM-41 catalysts and investigate isomerization of 1-butene to isobutene.

2. Experimental

2.1. Catalyst synthesis and characterization

The Na-MCM-41 mesoporous molecular sieve was synthesized in the laboratory using the method mentioned in [18] with some modifications. Synthesis was performed in a 300 ml autoclave at 373 K using tetradecyltrimethylammonium bromide (Aldrich) as a surfactant, sodium silicate solution (Merck) as a source of silica and sodium aluminate (Riedel-Häen) as a source of alumina. The synthesized material was washed thoroughly with distilled water, dried at 383 K and calcined in an oven to remove surfactant at 813 K. The Na-MCM-41 mesoporous material was ion-exchanged with 1 M NH_4Cl, washed with distilled water to remove chloride ions and dried at 373 K. H-MCM-41 was obtained by calcination of NH_4-MCM-41 in an oven at 803 K. Cu–H-MCM-41 was prepared by ion-exchange of H-MCM-41 using copper nitrate solution, washed with distilled water, dried at 373 K and calcined at 773 K.

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The characterization of Na-MCM-41 was carried out using an X-ray powder diffractometer (Philips pW 1800), X-ray fluorescency (Siemens), and a Sorptometer 1900 (Carlo-Erba Instruments). The acidic properties of H-MCM-41, Na-MCM-41 and Cu–H-MCM-41 catalysts were investigated using FTIR (diffuse reflectance) of adsorbed pyridine. The content of copper in Cu–H-MCM-41 was determined by a direct current plasma (DCP) spectrometer. The hydrogen and oxygen pre-treated Cu–H-MCM-41 catalysts were analyzed by X-ray powder diffraction.

2.2. Catalytic experiments

The catalytic properties of H-MCM-41, Na-MCM-41 and Cu–H-MCM-41 in the isomerization of 1-butene were studied in a fixed-bed microreactor at near atmospheric pressure. The product analyses were carried out on-line using a gas-chromatograph (Varian 3700) equipped with a flame-ionization detector (FID) and a capillary column (50 m × 0.32 mm ID fused silica PLOT Al_2O_3–KCl). The influence of pre-treatment of Cu–H-MCM-41 catalyst with oxygen or hydrogen on the conversion of 1-butene, yield of isobutene and selectivity to isobutene was investigated at 673 K with WHSV 30 h^{-1}. Pre-treatment of the Cu–H-MCM-41 catalyst with synthetic air or hydrogen was carried out at 773 K for 2 h and designated as Cu–H-MCM-41-Ox and Cu–H-MCM-41-Red, respectively. The conversion of 1-butene, yield of isobutene and selectivity to isobutene over H-MCM-41, Na-MCM-41, Cu–H-MCM-41-Ox and Cu–H-MCM-41-Red catalysts as functions of time on stream were investigated at 673 K with WHSV of 30 h^{-1}. The WHSV of 30 h^{-1} was chosen to keep the conversion of 1-butene below 35%. The conversion of 1-butene, selectivity to isobutene and yield of isobutene were defined as follows:

$$\text{conversion (mass\%)} = \frac{(Q_\text{m})_{\text{1-butene, in}} - (Q_\text{m})_{n\text{-butenes, out}}}{(Q_\text{m})_{\text{1-butene, in}}} \times 100,$$

$$\text{selectivity to isobutene (mass\%)} = \frac{(Q_\text{m})_{\text{isobutene, out}}}{(Q_\text{m})_{\text{1-butene, in}} - (Q_\text{m})_{n\text{-butenes, out}}} \times 100,$$

$$\text{yield of isobutene (mass\%)} = \frac{(Q_\text{m})_{\text{isobutene, out}}}{(Q_\text{m})_{\text{1-butene, in}}} \times 100.$$

3. Results and discussion

3.1. Characterization results

The X-ray powder diffraction pattern of the Na-MCM-41 after removal of surfactant was similar to those reported in the literature [19], indicating the synthesis of pure structure of MCM-41 with long range hexagonal ordering of the channels. Copper-modified MCM-41 also indicated XRD pattern characteristic of MCM-41. The BET surface area of Na-MCM-41, H-MCM-41, Cu–H-MCM-41-Ox and Cu–H-MCM-41-Red fresh catalysts was determined by nitrogen adsorption and was found to be highest for unmodified Na-MCM-41 (table 1). The X-ray powder diffraction patterns and very high surface areas exhibited by the synthesized catalysts confirmed that the materials were of MCM-41 type and that surfactant had been completely removed from the channels. The Si/Al ratio of Na-MCM-41 was analyzed to be 2.6. The FTIR spectra of adsorbed pyridine showed the presence of Brønsted and Lewis acid sites in the H-MCM-41, Na-MCM-41 and Cu–H-MCM-41 catalysts (figure 1). The content of copper in Cu–H-MCM-41 was determined to be 2.3 wt%.

Table 1
Surface area of fresh catalysts Na-MCM-41, H-MCM-41, Cu–H-MCM-41-Ox and Cu–H-MCM-41-Red

Catalyst	Surface area (m^2/g)
Na-MCM-41	1094
H-MCM-41	904
Cu–H-MCM-41-Ox	798
Cu–H-MCM-41-Red	658

3.2. Effect of pre-treatment of Cu–H-MCM-41 with synthetic air or hydrogen on the conversion of 1-butene, yield of isobutene and selectivity to isobutene

Isomerization of 1-butene was carried out over synthetic air pre-treated Cu–H-MCM-41-Ox and hydrogen pre-treated Cu–H-MCM-41-Red at the temperature of 673 K with WHSV 30 h^{-1}. The main products obtained over Cu–H-MCM-41-Ox after 10 min on stream (TOS) were methane, ethane, ethene, propene, isobutane, *n*-butane, isobutene, *cis*-

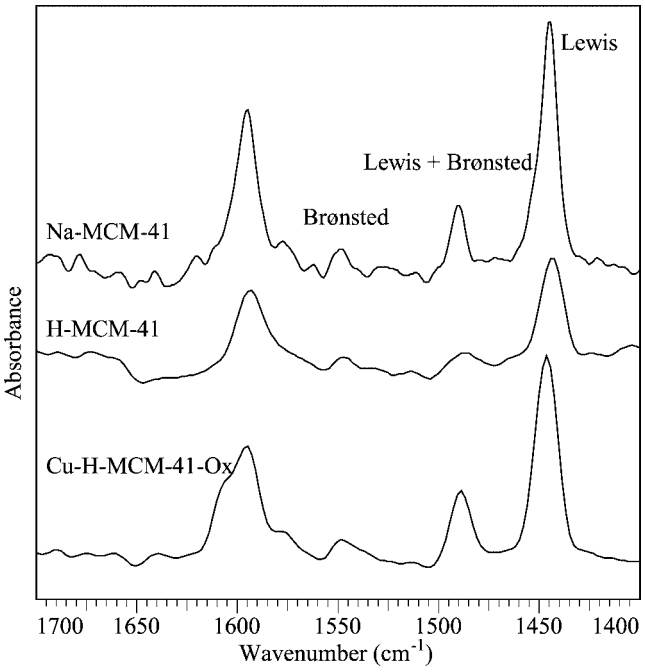

Figure 1. FTIR spectra of adsorbed pyridine on Na-MCM-41, H-MCM-41 and Cu–H-MCM-41-Ox catalysts.

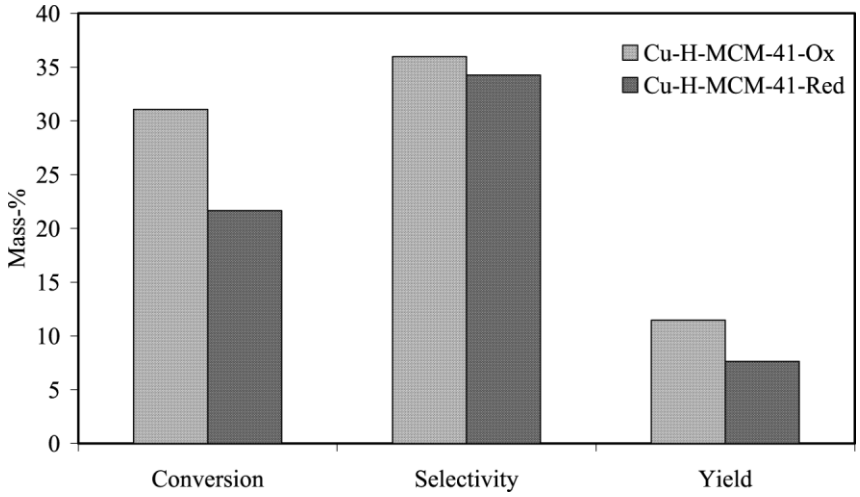

Figure 2. Conversion of 1-butene, selectivity to isobutene and yield of isobutene at 673 K with WHSV 30 h^{-1} after 10 min of time on stream (TOS) over oxidized Cu–H-MCM-41-Ox and reduced Cu–H-MCM-41-Red catalysts.

2-butene, *trans*-2-butene, pentenes and octenes. The synthetic air pre-treated Cu–H-MCM-41-Ox catalyst exhibited higher conversion of 1-butene, selectivity to isobutene and yield of isobutene than the hydrogen pre-treated Cu–H-MCM-41-Red (figure 2). The amount of alkanes (methane, ethane, propane and isobutane) formed over Cu–H-MCM-41-Ox is also higher than over Cu–H-MCM-41-Red. The reason for higher conversion of 1-butene over Cu–H-MCM-41-Ox is the presence of highly dispersed forms of Cu^{2+} and Cu^{+}. Highly dispersed copper species and acid sites of MCM-41 form active sites for 1-butene isomerization. Copper species, besides introducing Lewis acid sites, act as dehydrogenating agents for alkanes formed during the reaction and thereby generating reactive olefin intermediates which undergo oligomerization and cracking reactions. The explanation for lower conversion of 1-butene is the presence of copper in Cu–H-MCM-41-Red in the form of Cu^{0} due to the reduction of copper species by hydrogen. Copper in metallic form is not active in the 1-butene isomerization reaction and most of the activity is due to the presence of acid sites in Cu–H-MCM-41-Red. However, some copper species could be in the form of Cu^{+}, since it is very difficult to reduce this form of copper to Cu^{0}. The good stability of Cu^{+} and easy reducibility of Cu^{2+} in Cu-ZSM-5 zeolite has been reported [20]. The presence of Cu^{0} species in Cu–H-MCM-41-Red was confirmed by the X-ray powder diffraction technique.

The X-ray powder diffraction technique has been used to identify CuO and Cu^{0} in the copper-modified zeolite catalysts. It has been reported in the literature that the Cu-ZSM-5 catalyst, overexchanged with Cu, exhibits a peak at the 2θ value of 38.6, which is attributed to the presence of CuO [21]. The X-ray powder diffraction pattern of Cu–H-MCM-41-Ox did not exhibit the peak for CuO at the 2θ value of 38.6, indicating the absence of copper in the form of oxide. However, the XRD pattern of Cu–H-MCM-41-Red showed a peak at 2θ with a value of 43.4, which is attributed to the presence of copper in the form of Cu^{0}. Hence, most of the copper in Cu–H-MCM-41-Ox is assumed to be present in the form of Cu^{2+} or Cu^{+}, as there was no peak at the 2θ value of 43.4. The ion-exchange property of MCM-41 also promotes the stabilization of copper in the form of highly dispersed Cu^{2+}. Presence of Cu^{+} in MCM-41 can be attributed to autoreduction of Cu^{2+} to Cu^{+} during the thermal pre-treatment of Cu–H-MCM-41. The detailed investigations regarding the different states of copper in MCM-41 using different techniques are underway and will be discussed in a forthcoming paper.

3.3. Role of Cu in MCM-41 for the conversion of 1-butene, yield of isobutene and selectivity to isobutene

The copper-modified Cu–H-MCM-41-Ox and Cu–H-MCM-41-Red exhibited higher conversion of 1-butene and yield to isobutene than unmodified H-MCM-41 and Na-MCM-41 catalysts (figures 3 and 4). The reason for such catalytic behavior of unmodified H-MCM-41 and Na-MCM-41 is the mild acidic property and mesoporous structure of these catalysts which are not very favorable for 1-butene isomerization. Hence, introduction of copper species in MCM-41 enhances the acidic properties and inserts a bifunctional character to MCM-41, which is conducive to the reaction of 1-butene isomerization. The reaction path over Cu–H-MCM-41-Ox is dehydrogenation of alkanes produced during the reaction over copper species followed by oligomerization, mild cracking and isomerization of 1-butene over acid sites. The 1-butene isomerization reaction path over H-MCM-41 and Na-MCM-41 is proposed to be dimerization of 1-butene followed by mild cracking and oligomerization, resulting in lower conversion of 1-butene and yield of isobutene. The H-MCM-41 catalyst was slightly better in conversion and yield of isobutene than Na-MCM-41. Although acidity is not introduced in the Na-MCM-41 by post synthesis modification using ion-exchange of Na by NH_4, the acidity in this catalyst is introduced during calcination of the organic surfactant which is an ammonium compound,

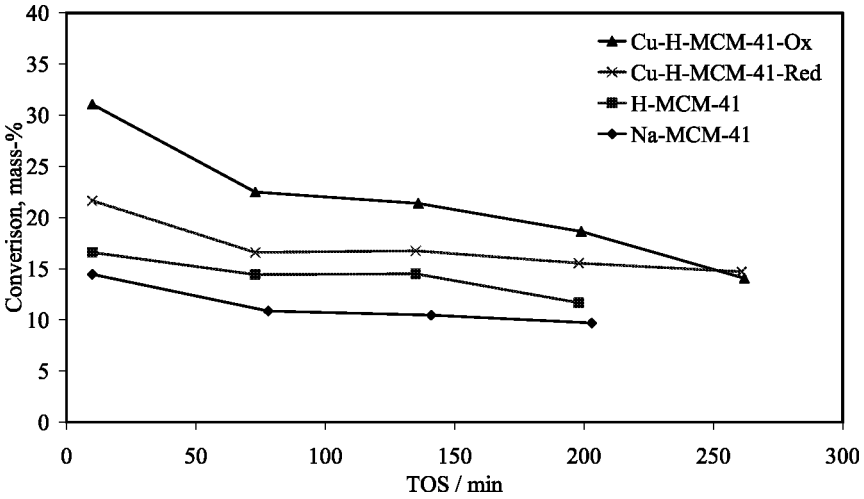

Figure 3. Conversion of 1-butene as a function of time on stream at 673 K with WHSV 30 h^{-1} over Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 catalysts.

thus leaving behind protons. We have observed similar behavior for the as synthesized K-ZSM-22 and H-ZSM-22 in 1-butene isomerization [22]. The presence of Brønsted and Lewis acid sites in Na-MCM-41 was confirmed by FTIR of pyridine adsorption.

3.4. Time on stream (TOS) as a function of conversion of 1-butene, yield of isobutene and selectivity to isobutene over Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 catalysts

The Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 catalysts exhibited a decrease in conversion of 1-butene and yield of isobutene with time on stream (figures 3 and 4). Cu–H-MCM-41-Ox exhibited the highest selectivity to isobutene after 260 min (figure 5); however, conversion of 1-butene was low. The catalysts exhibited rapid deactivation at an early stage of the reaction. However, the extent of deactivation varied depending upon the type of catalyst. Cu–H-MCM-41-Ox and Na-MCM-41 catalysts pre-treated with oxygen exhibited very high deactivation. The reason for high deactivation over this catalyst is coke deposition and reduction in the state of active copper Cu^{2+} or Cu^{+} to metallic copper. The X-ray powder diffraction pattern of deactivated Cu–H-MCM-41-Ox catalyst exhibited two large peaks at 2θ values of 43.29 and 50.43 which is attributed to the presence of Cu^{0}. The main explanation for large peaks due to metallic copper in Cu–H-MCM-41-Ox deactivated catalyst is due to increased reduction of copper species in the presence of carbonaceous residues, which act as reducing agents and thereby increase the degree of reduction during reaction. The BET surface area of Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 used was found to be lower than for the fresh catalysts (tables 1 and 2). The reason for the decrease in the surface area is coke formation in the pores and channels of the catalysts. However, in copper-modified MCM-41 pore blockage can also occur due to the migration of loosely bounded metallic copper to the pore mouth.

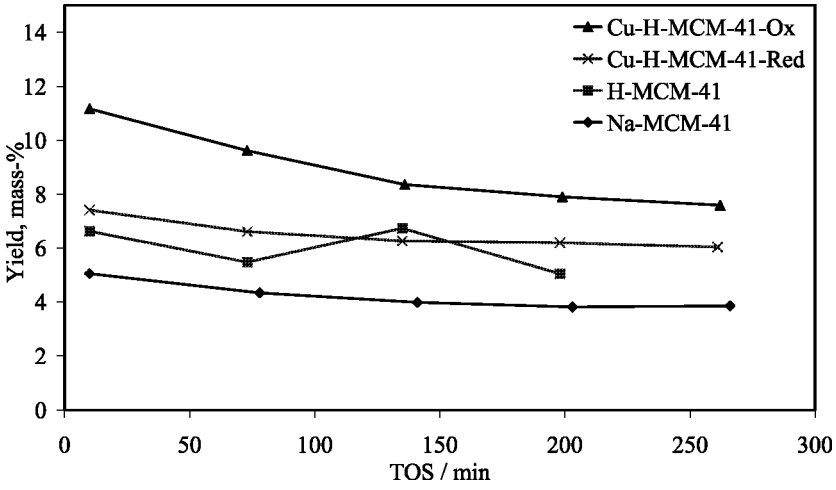

Figure 4. Yield of isobutene as a function of time on stream at 673 K with WHSV 30 h^{-1} over Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 catalysts.

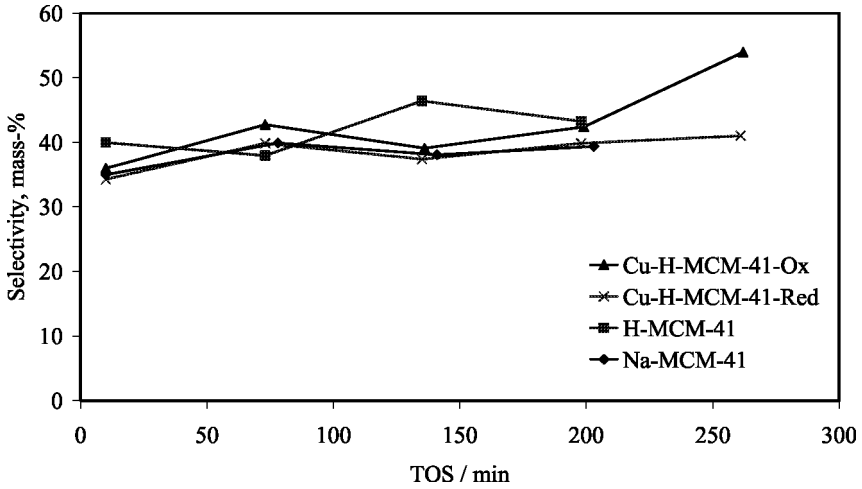

Figure 5. Selectivity to isobutene as a function of time on stream at 673 K with WHSV 30 h^{-1} over Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 catalysts.

Table 2
Surface area of deactivated catalysts Na-MCM-41, H-MCM-41, Cu–H-MCM-41-Ox and Cu–H-MCM-41-Red

Catalyst	Surface area (m^2/g)
Na-MCM-41	886
H-MCM-41	281
Cu–H-MCM-41-Ox	370
Cu–H-MCM-41-Red	593

4. Conclusions

Na-MCM-41, H-MCM-41 and Cu–H-MCM-41 mesoporous molecular sieve catalysts synthesized in the laboratory were highly phase pure MCM-41 as confirmed by different characterization techniques. Copper modified MCM-41 exhibited higher conversion of 1-butene and yield of isobutene than H-MCM-41 and Na-MCM-41 mesoporous molecular sieve catalysts. Copper species, Cu^{2+} and Cu^{+}, in the vicinity of acid sites are proposed to be the active centers for isomerization of 1-butene over oxygen pre-treated Cu–H-MCM-41-Ox. Copper cations introduce Lewis acidity in the MCM-41 structure and enhance the dehydrogenation of alkanes formed during the reaction of 1-butene isomerization. The pre-treatment of copper-modified MCM-41 catalysts by oxygen or hydrogen was observed to influence the conversion of 1-butene, yield of isobutene and selectivity to isobutene. Cu–H-MCM-41-Red pre-treated with hydrogen exhibited lower conversion of 1-butene and yield to isobutene than the Cu–H-MCM-41-Ox pre-treated with synthetic air. The reduction of copper species to Cu^0 in the hydrogen pre-treated Cu–H-MCM-41-Red was the main reason for the decrease in 1-butene conversion and yield of isobutene. The XRD pattern of Cu–H-MCM-41-Red confirmed the presence of Cu^0. The main reasons for Cu–H-MCM-41-Ox catalyst deactivation were coke formation and reduction of copper cations to metallic copper. The presence of metallic copper in deactivated Cu–H-MCM-41-Ox was indicated by XRD. The Cu–H-MCM-41-Ox, Cu–H-MCM-41-Red, H-MCM-41 and Na-MCM-41 deactivated catalysts exhibited lower surface area than the fresh catalysts due to coke formation in the channels of the catalysts.

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