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HZSM-5 supported silica-zirconia and its application in one-step synthesis of methyl isobutyl ketone

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1. Introduction

Methyl isobutyl ketone (MIBK) is a kind of important product which is extensively used as a solvent in paints, resins and coatings, as well as an extracting agent [1]. Traditionally, MIBK is manufactured via a three-step process: (1) aldol condensation of acetone to diacetone alcohol (DAA), (2) dehydration of DAA to mesityl oxide (MO), (3) hydrogenation of MO to MIBK [2]. All the three reactions can be carried out in a single step over bifunctional catalysts, which have attracted extensive interests [3–5]. One-step synthesis of MIBK reaction was typically studied using fixed-bed tubular reactors at atmospheric pressure and temperatures that rarely exceed 473 K [6]. The investigated bifunctional catalysts were consisted of Pd or Pt as hydrogenation component and acid or base support material which included various kinds of molecular sieves (ZSM-5 [7-9], X-zeolite [10,11], SAPO-11 [12]), mixed oxides [1,13,14], calcium hydroxyapatite [15], active carbon [6,16], etc.

HZSM-5 was studied as support in this reaction with various kinds of modifications. Good results were obtained at high pressure when treated with alkaline metal cations [17] or organic acid [18] in which acid strength or pore structure was modified. Zr–Si mixed oxide has attracted great research attentions for using as catalyst or support in acid-catalyzed reactions, such as alcohol

ABSTRACT

In order to adjust the acidity and texture property of HZSM-5, SiO_2-ZrO_2 was introduced via a modified sol-gel method. Pd-loaded catalyst was prepared and its catalytic activity was tested in one-step synthesis of MIBK. The catalyst exhibited a significant activity of acetone conversion up to 33.4% and MIBK selectivity up to 88.1% under atmospheric pressure. The acidity and textural properties of support material, as well as palladium dispersion of Pd-loaded catalyst were characterized. The results indicated that the proper acid strength and textural property of the support, together with the high dispersion of palladium resulted in good catalytic performance.

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dehydration [19], alcohol oxidation [20] and cycloalkane oxidation [21]. However, researches of Zr–Si oxide used in condensation reactions have not been reported. Among different preparation techniques, sol–gel was often used for its good control of the properties of the resulted material. Here, the mixed oxide and HZSM-5 were compounded by a modified sol–gel method in order to obtain an effective support material for synthesis of MIBK at atmospheric pressure. The Pd-loaded catalysts were prepared and demonstrated excellent catalytic activity in one-step synthesis of MIBK.

2. Experimental

2.1. Catalyst preparation

Before utilization, the as-received HZSM-5 (labeled as HZ) was calcined at 823 K for 5 h. The Zr–Si sol was prepared as follows: solution A containing 0.06 mol tetraethyl orthosilicate (TEOS) and 17 mL ethanol was added dropwise to solution B which was consisted of 0.02 mol ZrOCl₂·8H₂O and 17 mL distilled water at 313 K. Then HZ powder (3.621 g) was added in after aging for 30 min. The mixture became very ropy after 5 h. At last, it was dried at 383 K for 12 h and calcined at 823 K for 4 h. The obtained material was denoted as ZrSiHZ. SiO₂–ZrO₂ was synthesized by sol–gel method. Firstly, Zr–Si sol was prepared. After aging for 30 min, the temperature was increased to 343 K and gelation occurred immediately. The gel was dried and calcined. For comparison, physical mixture (PM) of SiO₂–ZrO₂ and HZ with the same



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ratio of ZrSiHZ was prepared by grinding. Palladium-loaded catalysts were prepared by the conventional wetness impregnation method using PdCl₂ solution with palladium loading of 0.3 wt%. The material was then dried at 393 K and calcined at 823 K for 4 h. Before reaction, raw catalysts were formed into particles of size 0.29–0.84 mm and reduced by hydrogenation at 573 K for 4 h.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained by Philips X Pert Pro X diffractometer operated with a Ni-filtered Cu K α radiation. Physisorption of N₂ at 77 K was carried out on ASAP 2020 apparatus. NH₃-TPD was performed on AutoChem II 2920 instrument. Typically, a sample of 100 mg was first pretreated in helium at 823 K for 30 min. Then temperature was cool to 373 K and the sample was saturated with ammonia. Desorption of ammonia was then carried out from 372 to 973 K under flowing helium (30 mL/min) using a temperature ramp of 10 K/min. High Resolution Transmission electron microscopy (HRTEM) was performed on JEM-2010 apparatus operating at 200 kV.

2.3. Catalytic activity test

The reactions were carried out in a fixed-bed micro-reactor (6 mm i.d.) using 0.6 g catalyst at ambient pressure. Acetone and H_2 were fed into the reactor from the top and mixed in preheating section. The acetone (0.02 mL/min) and H_2 were introduced with the molar ratio of H_2 and acetone fixed at 1. Before reaction, the catalyst was pretreated with hydrogen (20 mL/min) in situ at 453 K for half an hour and the experiment was carried out at this temperature for 2 h. The products were collected in a cold trap (held in an ethanol-dry ice bath) and quantified by GC equipped with a flame ionization detector.

3. Results and discussion

3.1. Characterizations

The XRD patterns of different samples are shown in Fig. 1. Different from that of PM, the pattern of ZrSiHZ just exhibited diffraction peaks of HZSM-5 with much lower intensity which suggested that SiO_2 -ZrO₂ was highly dispersed on surface of HZ. It was reported that high degree mixing of Zr–Si mixed oxide often led to absence of XRD pattern for ZrO₂ [22]. The broad peak around 22° (2 θ) seen from the smaller inset could be attributed to insertion of Zr into



Fig. 1. XRD patterns of materials: (A) HZ, (B) SiO₂-ZrO₂, (C) ZrSiHZ and (D) PM.

the framework of amorphous SiO₂. When SiO₂–ZrO₂ was synthesized on surface of HZ by sol–gel method, the mixed oxide was proved to be X-ray amorphous for the high mixing degree. In addition, the dealumination of HZSM-5 in ZrSiHZ which was proved by ²⁷Al-NMR spectra (not shown) may also relate to the decreased diffraction intensity. Besides a well-resolved peak at about 55 ppm due to tetrahedral framework aluminum (FAL), there was a small peak near 0 ppm attributed to octahedral extra-framework aluminum (EFAL) [23] in the ²⁷Al-NMR spectra of HZ and ZrSiHZ. A simple integration of the peaks was applied to determine the relative amount of the two species. The ratios of FAL to EFAL were: HZ-1:0.02 and ZrSiHZ-1:0.05. A stronger signal of EFAL existed in spectrum of ZrSiHZ, which implied that dealumination occurred.

The results from N_2 physisorption of the samples are given in Table 1. SiO₂–ZrO₂ was proved to be a kind of mesoporous material and possessed only a few micro-pores. Compared with HZ, introduction of SiO₂–ZrO₂ led to the decrease of surface and pore volume of ZrSiHZ and PM. Both the surface area and pore volume of ZrSiHZ were lower than that of PM which may be related to the amorphous SiO₂–ZrO₂ in ZrSiHZ. Combined with the above mentioned dealumination, the blockage of the EFAI species in the pore channels was also accounts for the decreased pore volume, especially in micro-pores [24].

Fig. 2 shows the NH₃-TPD traces of different materials. There were two peaks on NH₃-TPD spectrum of HZ: low-temperature peak (l-peak) found at about 450 K and high-temperature peak (h-peak) found at about 670 K. The spectrum of SiO₂-ZrO₂ exhibited a low broad peak indicating of less acid sites due to formation of Zr-O-Si [19]. Two desorption peaks were also observed on curves of ZrSiHZ and PM. The h-peak of PM found at 650 K suggested the decreased acid strength, which was due to dilution of strong acid sites by SiO₂-ZrO₂. Compared with that of PM, acid strength of ZrSiHZ, expressed by the corresponding temperature of peaks, especially strong acid strength, weakened distinctly while

Table 1				
「extural	properties	of	materials.	

Sample	$S_{\rm BET}^{a}$ (m ² /g)	$V_{\rm pore}^{b} (\rm cm^3/g)$	$V_{\rm micr}^{\rm c} (\rm cm^3/g)$
HZ	373	0.229	0.123
SiO ₂ -ZrO ₂	82.2	0.046	0.004
ZrSiHZ	187	0.098	0.065
PM	263	0.137	0.095

^a BET surface area.

^b Single point total pore volume at $P/P_0 = 0.97$.

^c Cumulative volume by H-K method.



Fig. 2. NH₃-TPD profiles of samples: (A) HZ, (B) SiO₂-ZrO₂, (C) ZrSiHZ and (D) PM.

weak acid sites and its strength changed insignificantly. Since the EFAL did not contribute to the acidity [25], the weak of strong acid strength of the ZrSiHZ can be ascribed to the dealumination in preparing procedure. Meanwhile, the coverage of surface of HZ by amorphous SiO₂–ZrO₂ may be another reason for the reduction of the acid sites.

Typical HRTEM images of the catalysts are shown in Fig. 3. The palladium was highly dispersed on surface of HZ. Whereas image of Pd/SiO_2-ZrO_2 showed that palladium was distributed as large particles (2–7 nm) in meso-pores. The presence of worm-like meso-pores confirmed the mesoporous texture of the SiO_2-ZrO_2

[26]. Large palladium particles cannot be found in images of Pd/ ZrSiHZ and Pd/PM, which implied that palladium species dispersed better than that of Pd/SiO₂–ZrO₂. But some palladium aggregated on surface of Pd/PM, which resulted in uneven distribution of palladium.

3.2. Acetone condensation

Activities of support materials and catalysts were tested under the same experiment conditions and the representative results were listed in Table 2. Pd/ZrSiHZ exhibited acetone conversion



Fig. 3. HRTEM images of catalysts: (A) Pd/HZ, (B) Pd/SiO₂-ZrO₂, (C) Pd/ZrSiHZ, (D) Pd/PM and (E) Pd/ZrSiHZ after used for 12 h.

Table 2						
Acetone	conversion	and	yield	of the	products. ^a	

Sample	Conversion (%)	Yield (%) ^b			
		MIBK	IPA	МО	DIBK
ZrSiHZ	5.7	0.9	_c	3.3	0.1
PM	8.0	0.2	0.5	5.0	-
Pd/HZ	9.2	8.2	0.1	0.5	0.1
Pd/ SiO ₂ -ZrO ₂	24.8	13.7	5.6	0.6	3.2
Pd/ZrSiHZ	33.4	29.4	0.2	-	0.9
Pd/PM	28.5	23.8	0.3	0.2	0.9

^a Reaction conditions: 453 K, 2 h, H₂/actone = 1, atmospheric pressure.

^b MIBK: methyl isobutyl ketone, IPA: isopropanol, MO: mesityl oxide, DIBK: diisobutyl ketone. Other byproducts: C5 (2-methyl-pentane), 2,6,8-trimethylnonane-4-one, isophorone and 4,6-dimethyl-2-heptanone, etc.

^c Can not determined.

and MIBK yield of 33.4 and 29.4%. This result compared well to those reported by other Refs. [2,4,11,13,15]. As the product of MO or MIBK condensed with another molecular of acetone, diisobutyl ketone (DIBK) was the major byproduct in gas-phase condensation [27]. Our catalyst was superior to others in terms of low yield of DIBK in gas phase acetone condensation.

When support materials were tested in absence of palladium, the condensation product MO was the major product with low acetone conversion, which proved the composed material acted mainly as acid catalysts. The Pd/HZ exhibited a low acetone conversion of 9.2%. Introduction of mixed oxide by different method resulted in the decreased acid strength of PM and ZrSiHZ. Accordingly, their Pd-loaded catalysts exhibited acetone conversion of 28.5 and 33.4%, respectively. This suggested that the relative weak acid strength was favorable for this reaction. Although ZrSiHZ showed lower surface area than that of PM, a higher MIBK yield of 29.4% was achieved by Pd/ZrSiHZ. The proper acidity of ZrSiHZ and more effective palladium dispersion of Pd/ZrSiHZ accounted for this phenomenon. In addition, SiO₂-ZrO₂ and HZ were mixed together in random in PM. Unlike that, the amorphous SiO₂-ZrO₂ dispersed on surface of ZrSiHZ which was favorable to the mass transfer.

Pd/SiO₂–ZrO₂ exhibited acetone conversion of 24.8% with yield of 5.6% isopropanol (IPA) and 3.2% DIBK. The high yield of IPA may be due to the large palladium particles of Pd/SiO₂–ZrO₂. Large pal-



Fig. 4. Acetone conversion and product selectivity versus time on stream over Pd/ ZrSiHZ.

ladium particles preferred to the hydrogenation of C=O of acetone to IPA in the competition between hydrogenation and condensation. This phenomenon was consistent with the Ref. [5] in which high Pd-loading resulted in high selectivity of IPA. Moreover, the absence of micro-pores can explain the higher yield of DIBK which was often formed in large pores.

The stability of Pd/ZrSiHZ was evaluated and the result was shown in Fig. 4. The catalytic activity of Pd/ZrSiHZ declined in 10 h. From the HRTEM image of the used catalyst (Fig. 3E), the aggregation of palladium may be the main reason for the declined activity. The selectivity of IPA was increased for the enlargement of palladium. This result was consistent with high yield of IPA on Pd/SiO₂–ZrO₂. Effective methods of doping the palladium were in research and in hope of improving the stability of the catalyst.

4. Conclusion

A kind of potential carrier ZrSiHZ was prepared by compounding HZSM-5 and SiO_2 -Zr O_2 via a modified sol-gel method. The Pd/ZrSiHZ showed significant catalytic activity in one-step synthesis of MIBK. The results demonstrated that the catalytic performance of the bifunctional catalyst for synthesis of MIBK strongly depended on the textural properties and the acidity of the support material. It was considered that the selectivity of the IPA was related to the particle size of the supported palladium. Although the stability of the catalyst needed to be further improved, a good catalytic performance of Pd/ZrSiHZ had been realized. The consequent researches were on the way.

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