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Vapor-phase catalytic methylation of 1,1,1,3,3,3-hexafluoroisopropanol for the mass

production of 1,1,1,3,3,3-hexafluoroisopropyl methyl ether

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Graphical Abstract

Vapor-phase pollution-free and mass production of 1,1,1,3,3,3-hexafluoroisopropyl methyl ether using mixed oxides of Mg and Al as catalysts



- Highlights
- HFE-356mmz was prepared by vapor-phase methylation of HFiP over Mg-Al oxides

- Among the various Mg-Al oxides, 3/2Mg-Al₂ with medium acidity and medium basicity exhibits the highest catalytic activity
- This study provides new evidence of the acid-base synergism reaction mechanism
- The conversion/total activity for **HFiP** over 3/2Mg-Al₂ were 89.4%/0.94 mmol h⁻¹ m⁻²
- Mg-Al oxides is a good substitute of metal fluorides to catalyze the methylation of HFiP

Abstract: With the phasing-out of chlorofluorocarbons and hydrochlorofluorocarbons required by the Montreal and Kyoto Protocols, hydrofluoroethers (HFEs) are now considered to be promising alternatives due to their zero ozone-depletion and low global-warming potentials, and their significant capacities for use in heat-pump and cleaning-agent applications. However, the pollution-free and large-scale synthesis of HFEs has been a long-standing challenge. To address the issue, we previously reported a novel synthetic method for the large-scale production of 1,1,1,3,3,3-hexafluoroisopropyl methyl ether

(HFE-356mmz), a representative HFE, through the vapor-phase methylation of

1,1,1,3,3,3-hexafluoroisopropanol using metal fluorides as catalysts. In this work, mixed oxides of Mg and Al with various Mg/Al₂ ratios were employed as alternative catalysts; their abilities to promote the reaction were determined and the methylation mechanism was explored. All Mg-Al mixed oxides promoted the production of **HFE-356mmz**, albeit with different efficiencies, which were found to be determined by the surface acid-base properties of the catalysts. The results agree well with those obtained using metal fluorides as catalysts and provide new mechanistic evidence. Our study not only offers further evidence of the reaction mechanism, but also affords a more universal and operable process that uses more-common and less-expensive catalysts.

Keywords: 1,1,1,3,3,3-hexafluoroisopropylmethyl ether, vapor-phase methylation, Mg-Al mixed oxide

1. Introduction

To protect the stratospheric ozone layer and address global warming issues, the consumption and production of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) was phased out by the Montreal and Kyoto Protocols [1]. Thereafter, hydrofluoroethers (HFEs) were considered as promising substitutes for CFCs and HCFCs as they have zero ozone-depletion and low global-warming potentials, short atmospheric lifetimes, and are widely applicable [2-4]. Recently,

1,1,1,3,3,3-hexafluoroisopropylmethyl ether (**HFE-356mmz**), a member of the HFE family, has been attracting growing interest due to its significant capacity for use in high-temperature heat-pump fluids, detergents, solvents, and foam-blowing agents [5-7]. However, **HFE-356mmz** is very challenging to prepare on the large-scale, which has greatly hindered the promotion and application of this compound. Although **HFE-356mmz** was able to be prepared by the O-methylation of

1,1,1,3,3,3-hexafluoroisopropanol (**HFiP**) using (CH₃)₂SO₄, CH₃X (X = Cl, Br, I), or diazomethane as the methylating agent over an inorganic base [8-10], the inability to separate the base from the product, and the large amount of waste water produced hinders its industrial production.

To mass-produce **HFE-356mmz**, we developed a new synthetic method that involves the vapor-phase catalytic methylation of **HFiP** with dimethyl carbonate (**DMC**) as the methylating reagent and a metal fluoride as the catalyst [11]. This pollution-free, recyclable, and continuous process is very suitable for the industrial-scale mass production of **HFE-356mmz**. We found that the catalytic activity of the metal fluoride (AlF₃, MgF₂, CaF₂, SrF₂, and BaF₂) was determined by the Lewis acid-base properties of its surface and the total amount of acidic sites on the surface. Only MgF₂, which is moderately Lewis acidic and basic, exhibited excellent catalytic activity. Based on the acid-base effects of the catalysts and

the reported methylation reaction mechanism using **DMC** [12,13], we proposed a reaction mechanism for the catalytic methylation of **HFiP**.

Herein, to further verify the reaction mechanism and to explore the effectiveness of other catalysts that are less expensive and easier to synthesize, we prepared a series of mixed Mg-Al oxides with different Mg/Al₂ ratios as alternatives to metal fluoride catalysts, and studied their reactivities during the methylation of HFiP (Scheme 1). Mixed Mg-Al oxides were selected because they are inexpensive, easy to prepare, and have readily adjustable acid-base properties [14]. Moreover, Mg-Al mixed oxides are widely used in the catalytic methylation of phenol and its derivatives [13,15,16]. In addition, it was found that HFiP has good stability under the optimum reaction temperature (eg. 240 °C). Therefore, Mg-Al oxides catalyst can be used in this reaction. Since the acid-base properties of Mg-Al oxides are determined by both the chemical composition and the preparation procedure [17,18], we prepared the Mg-Al oxides in this study using the co-precipitation method but with various Mg/Al₂ (MgO:Al₂O₃) ratios. The effect of the Mg/Al₂ ratio on the surface acid-base properties of each catalyst and its catalytic performance were systematically investigated. A metal oxide with moderate acidity and basicity (3:2 Mg/Al₂ ratio) exhibited the best activity, in good agreement with the proposed mechanism. We believe that our study supports the proposed reaction mechanism. Replacing metal fluorides by metal oxides led to a more universal and operable reaction that can be practically used to mass-produce HFE-356mmz.



Scheme 1. Synthesis of HFE-356mmz through the vapor-phase methylation of HFiP using DMC over a Mg-Al-oxide catalyst.

2. Experimental Section

2.1 Preparing the Catalysts

The Mg-Al mixed oxides were prepared by the co-precipitation method [19]. Taking the Mg-Al mixed oxide with a 2:3 Mg/Al₂ ratio as an example, a typical preparation process includes: (1) dissolving Mg(NO₃)₂·6H₂O (25.6 g, 0.1 mol, Aladdin, > 99%) and Al(NO₃)₃·9H₂O (112.5 g, 0.3 mol, Aladdin, > 99%) in 500 mL of distilled water and stirring for 1 h, and then (2) slowly adding 5% ammonia solution to the solution at room temperature with constant stirring until pH 9.5 was reached. The resulting suspension was collected by vacuum filtration, washed with distilled water, and then dried at 120 °C for 12 h. The as-obtained solid was calcined at 400 °C (10 °C min⁻¹) for 4h and then at 500 °C for 4 h in a muffle furnace, after which it was ground and pelletized. MgO, Al₂O₃, and the other Mg-Al mixed oxides were all prepared following the same preparation procedure but with different molar ratios of Mg(NO₃)₂·6H₂O to Al(NO₃)₃·9H₂O. The as-prepared Mg-Al mixed oxides are labeled as "a/b Mg-Al₂", where "a/b" represents the molar ratio of MgO and Al₂O₃ in the mixed oxides; for example, "2/3Mg-Al₂" refers to the catalyst with a 2:3 ratio of MgO and Al₂O₃. The catalysts prepared in this manner were used directly in the vapor-phase methylation reaction.

2.2 Characterizing the Catalysts

The crystalline structures of all catalysts were examined by X-ray diffractometry (XRD) in the 10–90° 20 range on a Bruker D8 Advance diffractometer with Ni-filtered Cu K α radiation (λ = 1.540 Å). The Mg/Al₂ molar ratios were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on an Agilent ICP-OES 730 instrument.

Brunauer–Emmett–Teller (BET) surface areas were determined by N₂ physisorption using a Micromeritics TriStar II 3020 porosity analyzer. Prior to N₂ physisorption, each sample was degassed for 3 h at 250 °C. Surface areas were calculated according to the BET equation.

Catalyst acidities were determined by the temperature programmed desorption of NH₃ (NH₃-TPD) using a Quantachrome Autosorb-iQ-C (USA) instrument. Prior to the measurement, all the samples were vacuum dried at 400 °C for 8 h. After calcination, each sample (100 mg) was first heated in He (30 cm³ min⁻¹) at 250 °C for 1h and then treated with a 5% NH₃/He stream at 100 °C for 1h. Thereafter, the sample was flushed with He at 100 °C for 6 h to remove the weakly adsorbed NH₃. NH₃ was gradually liberated as the temperature was increased from 100 to 500 °C at 10 °C min⁻¹, and was detected by on-line gas chromatography (GC) with a thermal conductivity detector. To determine the basicities of the catalysts, they were subjected to CO₂-TPD in a manner similar to NH₃-TPD, with the exception that CO₂ was injected instead of NH₃.

2.3 Testing the Catalyst and Analyzing the Product

All of the catalysts (particles 0.8–1.2 mm in diameter, 20 g) were flushed with N₂ at 240 °C for 4 h before methylation. A mixture of **HFiP** (Sinochem, Lantian, > 99%) and **DMC** (Aladdin, > 99%) in a 1:2 molar ratio was fed into a down-flow reactor using a syringe pump, and the mixture was allowed to react at 240 °C and 101.1 kPa. The catalysts were tested at a contact time of 8 s by analyzing the outlet reaction mixture by GC using a GC-2014C chromatograph (Shimadzu). The GC instrument was fitted with a DB-VRX capillary column (30 m × 0.45 mm × 0.25 µm), whose temperature was first held at 50 °C for 5 min, and then heated to 200 °C at 10 °C min⁻¹, and finally held at 200 °C for 8 min. The injection port and the hydrogen flame ionization detector were maintained at a constant temperature of 200 °C. The

carrier gas (He) was introduced at 10 mL min⁻¹. The conversion (X_H) of **HFiP** and the selectivity (S_H) of **HFE-356mmz** were determined using a reported method [11].

3. Results and discussion

3.1 Activities of the Catalysts for the Methylation of HFiP

Despite the low catalytic activities of pure MgO and Al_2O_3 in the **HFiP** methylation reaction, all mixed Mg-Al oxides promoted the reaction efficiently. Since no by-products were detected in the outlet reaction mixture for any of these catalysts, the S_H for **HFE-356mmz** was considered to be 100% in all cases. However, the X_H of **HFiP** differed among the various Mg-Al oxides (Table 1), with 3/2Mg-Al₂ exhibited the highest activity.

Catalyst ^b Total activity d (mmol h⁻¹ m⁻²) XH^c (%) MgO 3.6 0.09 0.73 3/1Mg-Al₂ 48.9 2/1Mg-Al₂ 66.1 0.75 $3/2Mg-Al_2$ 89.5 0.94 0.70 $1/1Mg-Al_2$ 76.2 $2/3Mg-Al_2$ 70.9 0.56 $1/2Mg-Al_2$ 42.7 0.33 $1/3Mg-Al_2$ 29.0 0.20 7.9 γ-Al₂O₃ 0.04

Table 1. X_H data for the vapor-phase methylation of **HFiP** with **DMC** over various catalysts.^a

^aReaction conditions: temperature = 240 °C; contact time = 8 s; **HFiP** injection rate = 139.8 mmol h^{-1} ; running time = 4 h.

^bThe as-prepared Mg-Al mixed oxides are labeled as "a/b Mg-Al₂", where "a/b" represents the molar ratio of MgO and Al_2O_3 in the mixed oxides.

^cX_H (HFiP conversion) was determined by GC against a calibrated internal standard.

^dTotal activity (mmol $h^{-1} m^{-2}$) was determined from the molar reaction rate of **HFiP** and the specific surface area of the catalysts used in this reaction.

3.2 Characterization and Evaluation the Catalyst

To determine the reason for the different catalytic activities of the mixed Mg-Al oxides, the crystalline phases, surface areas, and surface acid-base properties of all catalysts were carefully investigated. Then, the 500 h lifetime of the optimized catalyst was evaluated and compared with that of MgF₂.

The crystalline phases of the catalysts were examined by XRD. As summarized in Table 2, Al₂O₃ and MgO exhibited γ -Al₂O₃ and MgO (cubic) phases, respectively. The XRD patterns of the Mg-rich mixed oxides (Entries 2–4, Table 2) exhibited typical diffraction peaks of MgO and γ -Al₂O₃, with the intensities of the MgO diffraction peaks observed to increase with increasing MgO content. On the contrary, the Mg-Al mixed oxides with larger Al contents (Entries 6-9, Table 2) only exhibited diffraction peaks typical of γ -Al₂O₃, suggesting that MgO is well dispersed in these γ -Al₂O₃ lattices. An additional MgAl₂O₄ phase was observed for 1/1Mg-Al₂ (Entry 5, Table 2), which is probably due to the transition from the Mg-rich to the Al-rich phase. Although the 1/3Mg-Al₂, 1/2Mg-Al₂, and 3/2Mg-Al₂ mixed oxides exhibited catalytic activity (Table 1) that increased with increasing γ -Al₂O₃-diffraction-peak intensity, the 1/2Mg-Al₂ oxide, which showed pure γ -Al₂O₃ diffractions, was much less active. Therefore, catalytic activity does not correlate with the intensities of the γ -Al₂O₃ diffractions. In addition, the 3/1Mg-Al₂ oxide that exhibited diffraction peaks from both MgO and γ -Al₂O₃, and the 1/1Mg-Al₂ oxide that showed diffraction peaks corresponding to the MgAl₂O₄ phase and γ -Al₂O₃, exhibited similar catalytic activities, which indicates that the nature of the Mg phase (MgO or MgAl₂O₄) has a negligible influence on activity. Therefore, we conclude that catalytic activity is not determined by the crystalline phase of the catalyst.

Entry	Catalyst ^a	Mg/Al ₂ molar ratio		Surface area	XRD structural analysis		
		Theoretical Measured ^b		$(m^2 g^{-1})$	Phases detected		
1	MgO	-	-	56.0	MgO periclase		
2	3/1Mg-Al ₂	3.0	3.4	93.9	MgO periclase + γ-Al ₂ O ₃		
3	2/1Mg-Al ₂	2.0	2.1	122.4	MgO periclase + γ -Al ₂ O ₃		
4	3/2Mg-Al ₂	1.5	1.6	133.2	MgO periclase + γ -Al ₂ O ₃		
5	1/1Mg-Al ₂	1.0	1.0	152.2	$MgAl_2O_4 + \gamma - Al_2O_3$		
6	2/3Mg-Al ₂	0.68	0.68	177.2	γ -Al ₂ O ₃		
7	1/2Mg-Al ₂	0.50	0.44	179.7	γ -Al ₂ O ₃		
8	$1/3Mg-Al_2$	0.33	0.31	205.4	γ -Al ₂ O ₃		
9	Al ₂ O ₃	-	-	264.5	γ-Al ₂ O ₃		

Table 2. BET surface areas and XRD data for MgO, Al₂O₃, and the Mg-Al mixed oxide samples.

^aThe as-prepared Mg-Al mixed oxides are labeled as "a/b Mg-Al₂", where "a/b" represents the molar ratio of MgO and Al₂O₃ in the mixed oxides.

^bMg/Al₂ molar ratios in the final precipitates were determined by ICP-OES.

The BET surface areas of the catalysts are listed in Table 2. Among these catalysts, γ -Al₂O₃ and MgO exhibit the largest (264.5 m² g⁻¹) and smallest (56 m² g⁻¹) surface areas respectively. The surface area of the Mg-Al mixed oxide was observed to decrease with increasing Mg content. Therefore, the surface properties of these catalysts can readily be tuned by adjusting the Mg content; however, the surface areas and catalytic activities do not correlate. Therefore, we conclude that the activity of the catalyst is not determined by its surface area.

The acidities of the catalysts were next studied by NH₃-TPD (Fig. 1). According to previous studies [20], NH₃-TPD peaks in the 80–150 °C, 150–300 °C, and 300–450 °C ranges correspond to weak (W), medium (M), and strong (S) acidities, respectively. The NH₃-TPD profile for Al₂O₃ displays two overlapping peaks at about 180 °C and 305 °C arising from NH₃ adsorbed at medium and strongly acidic sites; similar bands in the NH₃-TPD curves were observed for the Al-rich samples (Entries 5–9, Table 3). The NH₃-desorption temperature increased with increasing Al content. The desorption of NH₃ from the MgO and MgO-rich samples (Entries 1–4, Table 3) gave rise to weak bands below 170 °C, indicating the existence of sites with weak and medium acidities. The acid-site densities and percentage contribution of

each peak were determined by integrating the TPD profiles, the results of which are presented in Table 3. MgO exhibited the lowest total evolved NH₃, which increased with increasing Al content (Entries 1–9, Table 3). Moreover, the S peak contributed less with decreasing Al content, while the W peak contributed more, and the contribution of the M peak first increased and then decreased.



Fig. 1. NH₃-TPD profiles for the catalysts examined in this study.

The basicities of the catalysts were studied by CO₂-TPD, which revealed the existence of sites with different base strengths (Fig. 2). The desorption peaks at 80–150 °C, 150–300 °C, and > 300 °C are attributed to the desorption of CO₂ from the sites of weak (W), medium (M), and strong (S) basicities, respectively. The CO₂-TPD profile of MgO displays two broad peaks at about 320 °C and 220 °C, indicating the presence of sites of strong and medium basicity; similar peaks were observed for the Mg-rich samples (Entries 2–4, Table 3). The CO₂-desorption temperature was observed to decrease with decreasing Mg content. On the other hand, the CO₂-desorption temperatures of the Al₂O₃ and Al-rich samples (Entries 6–9, Table 3), decrease with increasing Al content, and only sites of medium and weak basicity were observed for the Al₂O₃, 1/3Mg-Al₂ and 1/2Mg-Al₂ samples. The total amount of desorbed CO₂ and the

percentage contribution of each peak determined by integrating the TPD profiles are presented in Table 3. In general, the contribution of the S peak decreased, while that of the W peak increased, and that of the M peak first increased and then decreased with increasing Al content (Entries 1–9, Table 3).

According to the acidity and basicity data for various catalysts, Al₂O₃ and MgO are dominated by strongly acidic and basic centers, respectively, while the mixed oxides contain both weakly acidic and basic centers as well as those of medium strength. When referring to the catalytic activities, we found that the 3/2Mg-Al₂ oxide contains the highest percentage of both medium-strength acidic centers (87.8%, Table 3) and medium-strength basic centers (70.6%, Table 3), which may contribute to this catalyst exhibiting the highest activity in the methylation reaction. Similarly, all other catalysts that show high catalytic activities, such as 3/1Mg-Al₂ oxide (0.73 mmol h⁻¹ m⁻², Table 1), 1/1Mg-Al₂ oxide (0.70 mmol h⁻¹ m⁻², Table 1), and 2/1Mg-Al₂ oxide (0.75 mmol h⁻¹ m⁻², Table 1), exhibit relatively high percentages of both medium-strength acidic and basic centers (Table 3). These results are in good agreement with those obtained using metal fluorides as catalysts [11].



Fig. 2. CO₂-TPD profiles for the catalysts examined in this study.

Entry	Catalyst ^a	Densities of acidic sites ^b (µmol m ⁻²)			Densities of basic sites ^c (µmol m ⁻²)				
		$\mathbf{W}^{d,e}$	$M^{d,e}$	$\mathbf{S}^{d,e}$	Total evolved NH ₃	W ^{d,e}	$\mathbf{M}^{d,e}$	S ^{d,e}	Total evolved CO ₂
1	MgO	0.15	0.07	0.0	0.22	0.77	3.89	3.78	8.44
		(68.9%)	(31.1%)	(0.0%)		(9.1%)	(46.1%)	(44.8%)	
2	3/1Mg-Al ₂	0.11	0.15	0.0	0.26	0.34	1.64	0.77	2.75
		(43.6%)	(56.4%)	(0.0%)		(12.3%)	(59.6%)	(28.1%)	
3	2/1Mg-Al ₂	0.15	0.36	0.0	0.51	0.20	0.90	0.22	1.32
		(28.5%)	(71.5%)	(0.0%)		(15.6%)	(68.1%)	(17.3%)	
4	3/2Mg-Al ₂	0.07	0.61	0.01	0.69	0.40	1.40	0.18	1.09
		(10.1%)	(87.8%)	(2.1%)		(20.3%)	(70.6%)	(9.1%)	1.98
5	1/1Mg-Al ₂	0.06	0.58	0.07	0.71	0.20	0.47	0.04	0.71
		(8.5%)	(81.7%)	(9.8%)		(28.6%)	(66.2%)	(5.2%)	
6	2/3Mg-Al ₂	0.04	0.72	0.14	0.90	0.46	0.49	0.03	0.98
		(4.6%)	(80.3%)	(15.1%)		(47.3%)	(49.6%)	(3.1%)	
7	1/2Mg-Al ₂	0.0	0.89	0.24	1.13	0.32	0.19	0.00	0.51
		(0.0%)	(78.8%)	(21.2%)		(63.6%)	(36.4%)	(0.0%)	
8	1/3Mg-Al ₂	0.0	0.60	0.47	1.07	0.59	0.26	0.0	0.85
		(0.0%)	(56.1%)	(43.9%)		(69.4%)	(30.6%)	(0.0%)	
9	Al ₂ O ₃	0.00	0.31	1.09	1.40	0.15	0.02	0.0	0.17
		(0.0%)	(22.4%)	(77.6%)		(90.5%)	(9.5%)	(0.0%)	0.17

Table 3. Acid-base surface properties of MgO, Al₂O₃, and Mg-Al mixed oxide samples

^aThe as-prepared Mg-Al mixed oxides are labeled as "a/b Mg-Al₂", where "a/b" represents the molar ratio of MgO and Al₂O₃ in the mixed oxides.

^bTPD of adsorbed CO₂.

°TPD of adsorbed NH₃.

^dW, weak; M, medium; S, strong.

^eThe percentage contribution of each peak is given in parentheses.

To compare the performance between 3/2Mg-Al₂ and MgF₂ (studied in our previous work), the 500

h lifetime of 3/2Mg-Al₂ was evaluated preliminarily. As shown in Fig. 3, the conversion of HFiP

decreased slowly from 89.5% to 83.2% with HFE-356mmz selectivity unchanged, which indicated that

3/2Mg-Al2 has a good stability in 500 h. Although the initial activity of 3/2Mg-Al2 (89.5%) is slightly lower

than that of MgF₂ (94.3%), 3/2Mg-Al₂ has the advantages of simple preparation and no use of corrosive HF,

so it still has good application value.



Fig. 3. The selectivity of **HFE-356mmz** (red dots) and conversion of **HFiP** (black squares) over 500 h. Reaction conditions: temperature = 240 °C; contact time = 8 s.

3.3 Reaction mechanism

In our previous work, we proposed a reasonable reaction mechanism for the vapor-phase methylation of **HFiP** using **DMC** over a metal fluoride [11]. Herein, the strong relationships between catalytic activity and surface acid-base properties using mixed Mg-Al oxides correlate well with those observed using metal fluorides, providing further support for the proposed acid-base synergistic mechanism.

In Mg-Al mixed oxides, the medium strength Lewis acid is attributed to the surface defect of Al³⁺ in Al³⁺-O²⁻-Mg²⁺ ion, while the medium strength Lewis base is assignable to the strong electronegativity O²⁻ [21,22]. Accordingly, a rational reaction mechanism of gas-phase methylation of **HFiP** and **DMC** catalyzed by Mg-Al binary catalyst is proposed in Scheme 2. Firstly, the carbonyl oxygen atom of **DMC** is adsorbed to the unsaturated coordination center of Al atom and **HFiP** is absorbed onto the O atom in Al³⁺-O²⁻-Mg²⁺ through hydrogen bonding.

Thereafter, the oxygen atom in HFiP attacks the methoxy carbon atom in DMC to produce

HFE-356mmz, with CO₂ and methanol liberated as volatile by-products and the catalyst regenerated. In addition, dimethyl ether was also formed through the condensation of methanol.



Scheme 2. Mechanism for the methylation of HFiP with DMC over mixed Mg-Al oxide.

This reaction mechanism well explains the strong activity of the catalyst with medium Lewis acidities and basicities (e.g., 3/2Mg-Al₂). Only catalysts with medium Lewis acidities and basicities facilitate the adsorption of both **DMC** and **HFiP**, as well as product desorption. If the catalyst is of strong Lewis acidity (e.g., Al₂O₃), the carbonyl oxygen of **DMC** is strongly adsorbed onto the catalyst [23]. On the other hand, if strong basic (e.g., MgO) or acidic molecules such as CO₂ or **HFiP** itself is strongly absorbed onto the catalyst [24], the catalyst activity would diminish seriously. Still, other mechanistic possibilities exist taking into account the strong affinity of the F-atoms in fluorocarbons with alumina based Lewis acids [25,26]. More experiments to further clarify the reaction mechanism are underway.

4. Conclusion

HFE-356mmz was successfully synthesized through the vapor-phase methylation of HFiP with DMC using Mg-Al mixed oxide catalysts instead of metal fluorides. Among various mixed Mg-Al oxides, the 3/2Mg-Al₂ oxide showed the highest catalytic activity due to its moderate Lewis acidity and basicity. The HFiP conversion and the activity of 3/2Mg-Al₂ were 89.4% and 0.94 mmol h⁻¹ m⁻², respectively, moreover, 3/2Mg-Al₂ gives good activity and stability in 500 h. The relationship between catalytic activity and the surface acid-base properties of the metal oxide catalyst were found to correlate well with those observed for metal fluorides, which provides further evidence of the acid-base synergistic mechanism involving activation of **DMC** at a Lewis acidic site through its carbonyl oxygen and activation of **HFiP** at an adjacent Lewis basic site through H-bonding. Our study provides deep insight into this reaction by unambiguously elucidating its reaction mechanism. Since the preparation of metal fluorides requires the use of HF, proving the applicability of metal oxides and confirming their comparable catalytic activity to that of metal fluoride make the reaction more universal and operable. The comprehensive mechanistic details provided, and our exploration of applicable catalysts for this reaction will promote the practical use of this chemistry for the pollution-free and large-scale production of HFE-356mmz.

Declaration of Conflict Interest

The authors declare that there is no conflict interest.

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